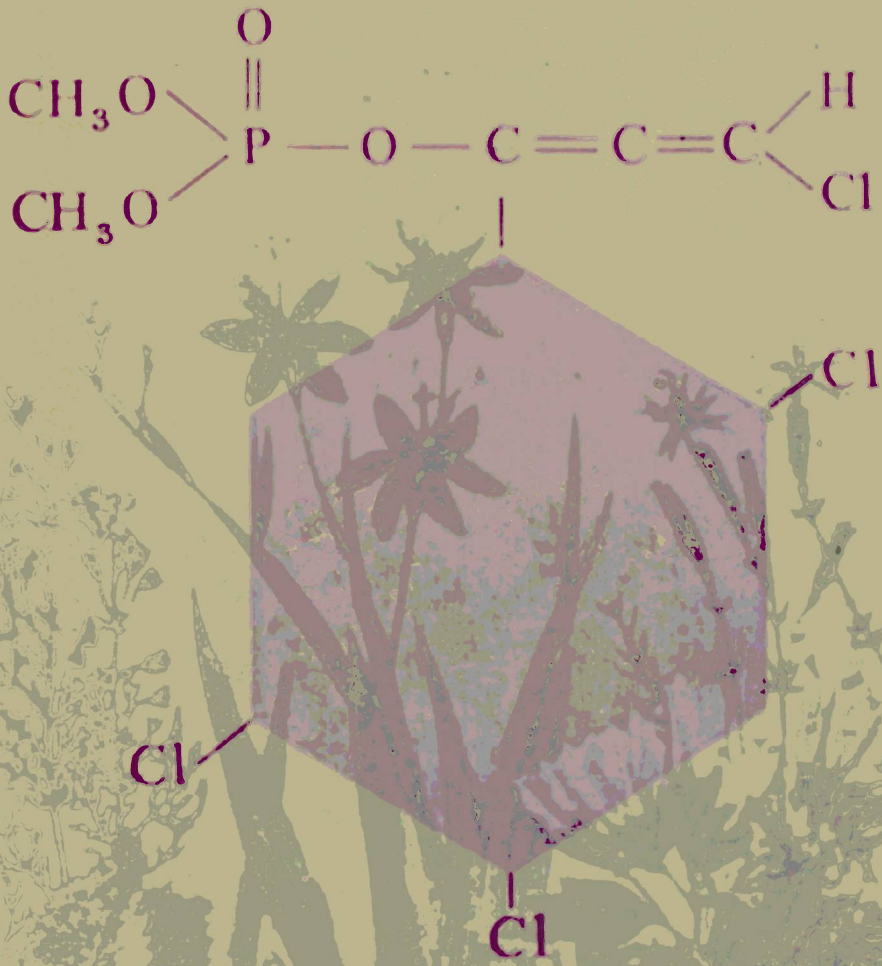
The Chemical Protection of Plants

G. S. GRUZDYEV, V. A. ZINCHENKO, V. A. KALININ, R. I. SLOVTSOV



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The Chemical Protection of Plants

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PREFACE

The present textbook is intended as a course in the chemical protection of plants for students of higher agricultural educational establishments. It will also be a helpful guide for agronomists of all specialities including agricultural chemists, plant protection agronomists, and agricultural specialists working in crop-growing in conditions of the expanding introduction of chemistry into agriculture.

The general part of the book treats the classification of modern pesticides, the fundamentals of agronomical toxicology, the influence of pesticides on the environment, and also the sanitary and physicochemical aspects of pesticide application.

The special part presents a detailed physicochemical characteristic of insecticides, rodenticides, fumigants, and also of herbicides and retardants, defoliants and desiccants, the features of their use, doses, periods and ways of application.

Information is also given on biological preparations of a bacterial and fungal origin and on antibiotics used to protect plants against diseases.

The combined and regional application of pesticides is also dealt with because the use of combined formulations and mixtures of pesticides with a different spectrum of action on harmful organisms is the most rational and economical way of protecting plants.

Georgi S. Gruzdyev

INTRODUCTION

An important reserve for raising productivity and increasing the gross output of agricultural products is the elimination of losses of the harvest due to pests, plant diseases, and weeds. Indeed, biological factors lead to losses of about 35% of the world's harvest. This figure includes 14% due to harmful animals and insects, 12% due to diseases, and 9% due to weeds. By groups of crops, these losses are 45% for sugar beets and sugar cane, 37% for coffee, cacao, tea, tobacco, and hops, 35% for cereals, 33% for oil bearing plants, 32% for potatoes, 32% for fibrous plants and rubber, 29% for fruits, and 28% for vegetables (N. Kramer, 1967).

The elimination of such significant losses is achieved by integrated pest management, including agrotechnical, quarantine, physical, mechanical, biological, and chemical methods.

Quarantine measures are introduced by the relevant authorities of a country to prevent the admission into it and spreading of the most dangerous plant diseases, pests, and weeds.

Quarantine measures acquire a constantly growing importance in conditions of the continuously increasing exchange of material and cultural values between states.

In the USSR, quarantine measures are carried out by the State Quarantine Inspection under the Ministry of Agriculture. All the union republics, autonomous republics, territories, and regions have quarantine inspections. They have at their disposal quarantine laboratories and nurseries, glasshouses, state botanical gardens, and also border quarantine detachments and fumigation teams. Scientific research in the field of the quarantine of plants is coordinated by the All-Union Research Institute of Plant Quarantine and Protection Technology.

Agrotechnical methods include measures aimed at providing better conditions for the growth and development of plants and improving their resistance to the action of harmful organisms. These measures include proper crop rotation, thorough tilling of the soil, preparation of the planting stock, the use of fertilizers balanced with respect to nutrient substances, the optimal periods and methods of sowing, harvesting, etc. Of special significance are varieties of agricultural crops resistant to a set of pests and diseases. A classical example of this is the creation by academician V. Pustovoit of a high oil-bearing variety of sunflower having a high resistance to a set of diseases and pests. At present, interspecific hybridization has been used to create the sunflower varieties Progress, Rassvet, and Novinka that resist diseases such as powdery mildew, gray mould, and verticilliaceous wilt. A number of varieties of winter wheat bred by academician V. Remeslo and other plant breeders resist the Hessian fly. Cotton varie-

ties of the Tashkent group exhibit resistance to verticilliaceous wilt. The cultivation of these varieties in combination with a set of agrotechnical, biological, and chemical measures of pest control facilitated an increase in the yield of cotton by 26-34%. The corn hybrids Dnepropetrovsky 247, Dnepropetrovsky 320, Krasnodarsky 300 and others are featured by their increased resistance to diseases.

As a result of selection for resistance to diseases, 17 varieties of sugar beets are being cultivated in the USSR that have an increased resistance to leaf spot, storage rot, erysifos, and blue mould. They include the varieties Yaltushkovskaya one-seeded, Yaltushkovsky hybrid, Pervomaisky hybrid, L'govsky hybrid, and improved Uladovskaya 752.

Varieties are being created with group and combined resistance. By group resistance is meant the resistance of varieties to several species of pests or pathogens, and by combined resistance, their resistance to both pests and diseases.

For example, the variety of spring wheat Saratovskaya 29 is relatively resistant to the rustic shoulder-knot moth, leaf beetle, frit fly, stalk rust, and loose smut, while the variety Kharkovskaya 46 is resistant to the rustic shoulder-knot moth, the frit and Hessian flies, grain aphids, stalk and brown rust. The varieties of winter wheat Mironovskaya-808 and Mironovskaya Yubileinaya created by academician V. Remeslo have a resistance to striple rust, powdery mildew, fusarial root rot, the Hessian fly, and the leaf beetle.

Great favour has been found by the highly productive varieties of barley Nutans 244, Odessky 36 and Chernomorets (selected by the All-Union Research Institute of Plant Breeding and Genetics), Chernigovsky 7 (selected by the Chernigov regional agricultural test station), Donetsky 4 (selected by the Donetsk regional agricultural test station), and Moskovskaya 121 (selected by the Scientific Research Institute of Agriculture of the Central Regions of the Non-Chernozem Zone), which have an increased resistance to helminthosporiosis, covered and loose smut, and the frit fly.

A proper scientifically substantiated crop rotation in which the system of alternating crops differing in their biological features is combined with a proper system of cultivating the soil and applying fertilizers makes it possible to eradicate weeds to a considerable degree and lower the infesting of plants by diseases and pests. The rotation of crops results in more complete utilization of the nutrient substances in the soil, water, and incorporated fertilizers.

The use of phosphorous-potassium and complete mineral fertilizers without a surplus of nitrogen lowers the infesting of cotton by bacterial blight and of grain and flax by rust, fusarial wilt, and other diseases.

The introduction of boron, manganese, zinc, copper, molybdenum, and other microelements lowers the infection of sugar beet by core

rot, of flax by bacteriosis, and prevents infection by certain virus diseases.

Soil liming facilitates the elimination of cabbage keel.

Physical methods are associated with the use of high and low temperatures, ultrasound, high-frequency currents, and radiation.

Mechanical methods consist in the extermination of insects using trap ditches, rings, light traps, and other contrivances.

The **biological method** of protecting plants is based on the use against pests, diseases, and weeds of their natural enemies, and also of various bacterial and fungal formulations causing the mass extermination of harmful insects. This method of plant protection is very promising because it is virtually safe to humans and animals and as a whole to the environment. For example, among the entomophags of harmful *Lepidoptera*, the egg parasite *Trichogramma* is widely used in the USSR by the method of seasonal colonization. The group of species and forms of parasites combined by this collective name is used for controlling turnip moths and cutworms on cereal, sugar beet, vegetable, cotton, and other crops, and also against corn borers, beet webworms, pea and codling moths.

A substantial recent achievement was the development of an industrial technology for breeding the *Trichogramma*. On the basis of this technology, the All-Union Institute of Plant Protection and the production organization "Agropribor" developed an experimental automated biological factory. At present, over 50 biological factories have been erected with a total output of over 50 000 million specimens during a single season (S. Andreev, G. Beglyarov, *et al*, 1981).

In addition to the *Trichogramma*, widespread use is made of a method of seasonal colonization of the predatory mite *Phytoseiulus persimila* to control spider mites on vegetable and decorative crops in sheltered soil. The use of this predator made it possible to sharply reduce, and in many cases to completely exclude the use of acaricides on the basic greenhouse crop—cucumbers. The yield from one square metre grows on an average by 1-5 kg in comparison with the use of acaricides. The scales of employing the *Phytoseiulus persimila* in the USSR are constantly growing, from 523 thousand square metres treated in 1970 to over 24 million treated in 1980 (S. Andreev, G. Beglyarov, *et al*, 1981).

To control aphids on cucumbers in greenhouses, the predatory gall midge aphidomiza is used. The simultaneous employment of the *Phytoseiulus persimilis* and the aphidomiza makes it possible to do without treatments with insectoacaricides.

The integrated protection of cucumbers is supplemented by the use against powdery mildew of the biological formulation trichothecin, which has no negative effect on the *Phytoseiulus persimilis*. The wooly aphid parasites (*Aphelinus mali*), introduced in the thirties, inhibit the reproduction of the wooly apple aphid very well in the

southern fruit-growing regions of the USSR. The specialized predator of the fluted scale, the rodolia (*Rodolia cardinalis* Muls.) has become acclimatized in Abkhazia, Adjaria, and the subtropical regions of the Krasnodar territory.

The use of microbiological means of plant protection has expanded. Two bacterial formulations are available on the market for controlling harmful *Lepidoptera*—entobacterin and dendrobacillin. The former is used against the cabbage and small white butterflies, diamond back and apple moths, pierid butterflies, brown-tail, fruit-tree tortrix, and fall web-worm moths. Dendrobacillin, in addition to the pests mentioned above, is effective against bollworms and armyworms.

Widespread field tests are successfully being conducted of the new bacterial formulation bitoxybacillin, developed on the basis of the *Bacillus thuringiensis* var. *thuringiensis* at the All-Union Research Institute of Agricultural Microbiology. Bitoxybacillin is toxic to the larvae of the Colorado beetle, the alfalfa weevil, phytonomus, cabbage maggots, turnip sawflies, bollworms, caterpillars of the turnip, cabbage, and silvery moths, and armyworms.

To control mouse-like rodents (*Muridae*), great favour is given in the USSR to the bacterial formulation bactorodencide, prepared in two forms—dry grains and dry amino-bone.

Among the fungal formulations, beauverin proposed by the Ukrainian Scientific Research Institute of Plant Protection on the basis of the *Beauveria bassiana* (Bals.) has passed state tests and may be used to control the Colorado beetle.

A formulation prepared on the basis of fungi of the genus *Ashersonia* has been tested against the greenhouse whitefly on vegetable crops in greenhouses and has shown good results.

The use of formulations based on antibiotics and microorganisms—antagonists—is very promising. Pilot lots of phytobacteriomycine are being produced that is effective against bacterioses of beans and soya and against root rots of wheat. The effectiveness of trichodermin prepared on the basis of the soil fungus-antagonist *Trichoderma lignorum* (Harr.) is being studied. The fungus produces a number of antibiotics having antibacterial and antifungal properties.

Trichodermin has shown good results against cotton wilt, wheat and cucumber root rots, sunflower and corn collar rot, and carrot black rot.

Broomrapes are being controlled with success by using the leaf-miner phytomyza (*Phytomyza orabanchia* Kalt.).

The use of phytomyzae in the Soviet Central Asian republics makes it possible to lower the infection of vegetable and melon crops and of tobacco plantations to an economically imperceptible level in three to five years (I. Bronstein, 1968, 1970).

The Russian knapweed nematode (*Paranquina picridis* Kir.) was

found to be the most effective herbiphag against the Russian knapweed (*Acroptilon picris*).

The **chemical protection of plants** is based on the use of various organic and inorganic compounds toxic to harmful organisms. The chemical means of plant protection (pesticides) are distinguished by their high universality. They can be used to control most pests, diseases and weeds on all agricultural crops and various lands, and also to treat granaries, storage bins, greenhouses, grain elevators, and other structures. The importance of fumigants for disinfecting various materials, food products, and fodder is exceedingly great. Pesticides can be applied with the aid of modern highly productive surface machinery and aircraft, with observance of all personal and public safety rules, and with account taken of measures for protecting the environment.

Pesticides for plant protection are produced by the chemical industry and marketed at comparatively low prices, which results in a high justification of their use. Every rouble spent on pesticides brings in 3-4 roubles worth of additional crop yield and the saving in the cost of caring for crops. The growth in the volume and quality of crop protection carried out in the USSR in 1976-1980 ensured an average annual preservation of the harvest estimated to cost over 7200 million roubles (V. Zakharenko *et al*, 1981).

At present, there is being developed and introduced into the farms of the USSR an integrated system of protecting cereal crops, oil-bearing plants, fibre-flax, rice, cotton, sugar beets, hemp, tobacco, potatoes, melons, leguminous plants, corn, clover, forest stands, and nurseries. The use of pesticides is especially effective in horticulture, where they make it possible to control exceedingly dangerous pests, improve the quality of the products, and substantially increase the yield of the fruits.

The use of herbicides is very effective. Many years of experience gained in this field show that herbicides appreciably lower the cost of controlling weeds and facilitate an increase in the yields of agricultural crops.

On fields of corn, sugar beets, sunflowers, soya, cotton, and flax, the use of herbicides in good time makes it possible to do without manual weeding, hoeing, and go over to an industrial technology of cultivating these time-consuming crops.

All the world's countries at present use about 1400 chemical compounds on whose basis tens of thousands of various formulations are produced. The total production of pesticides exceeds two million tonnes (of active ingredient).

Scientists predict that the world's rates of annual growth in the amount of pesticides produced will be 7.7% for herbicides, 6.2% for fungicides, 4.8% for insecticides, 7.1% for defoliants, desiccants, and plant growth regulators, and 6.4% for pesticides as a whole.

Protective measures with the use of chemical and biological means were carried out in 1980 in the USSR over an area of 162.6 million hectares, including plant pest and disease control on 89.5 million hectares (of which 17.5 million fell to the share of the biological method), weed control on 67.8 million, and defoliation and desiccation on an area of 5.3 million hectares. Of the total area, aerial treatment was used on 57 million hectares. The assortment of plant protection chemicals allowed to be used in the USSR in 1982-1985 includes 366 formulations, of which 12 are biological ones.

The plant service in the USSR is headed by the Ministry of Agriculture, subordinated to which is the All-Union production and scientific organization for catering to the agrochemical needs of agriculture ("Soyuzsel'khozkhimiya"). All the union republics have similar organizations.

The amalgamated service for the agrochemical catering to agriculture also incorporates the state service for plant protection, including 2000 district (interdistrict), regional (territorial), and republican plant protection stations, 1550 posts for signalling on and predicting the development of pests and diseases and diagnosis laboratories, 175 mechanized self-supporting detachments and 30 specialized expeditions and detachments for controlling locusts, gophers, mouselike rodents, and other mass and quarantine pests, 700 biological laboratories and factories for the reproduction and application of beneficial species (entomophags and microorganisms), and 102 control and toxicological laboratories. The total number of employees of this service is about 30 thousand, including over 16 thousand specialists with diplomas.

Scientific research in the field of controlling pests, plant diseases and weeds on a national scale is conducted by the plant protection department of the Lenin All-Union Academy of Agricultural Sciences, the All-Union Research Institute of Plant Protection, the All-Union Research Institute of Biological Methods of Plant Protection, and the Central Asian Institute of Plant Protection, as well as the plant protection institutes of the union republics. The production and research organization "Soyuzsel'khozkhimiya" is responsible for: the organizing in good time of measures for controlling pests and diseases of agricultural plants and of the application of chemical means of weed eradication; the state control of the carrying out by all farming organizations of the recommended measures for controlling pests and diseases of agricultural plants and weeds, the quality of this work, the strict observance of the established regulations for the application of pesticides; the control of the quality and timely delivery to agricultural organizations of chemicals, and the authenticity of the accounts and records of their utilization.

The studying, testing, and working out of recommendations for the use of chemical means of protection are coordinated by the

State Board for Chemical Means of Controlling Pests, Plant Diseases, and Weeds under the USSR Ministry of Agriculture.

Matters associated with a sanitary and hygienic assessment of pesticides are coordinated by the All-Union Research Institute of the Hygiene and Toxicology of Pesticides, Polymers, and Plastics. All pesticides permitted to be used on a large scale in the USSR are studied from their toxicological and hygienic aspects.

The conducted investigations underlie the working out of hygienic requirements to chemicals (a hygienic classification according to the degree of their toxicity) from the viewpoint of protecting the health of the population. Attention has grown in recent years to the strictly regulated application of pesticides excluding contamination of the environment and harm to beneficial organisms.

Fundamental changes have occurred in the assortment of pesticides, their forms and ways of application are constantly being improved, and the toxicity of the formulations to warm-blooded animals has been substantially diminished. If in 1960, the weighted mean toxicity of pesticides permitted to be used in the USSR was 147.5 mg/kg (LD_{50}), then in 1970 it was already 665 mg/kg, while in the last few years this figure has grown to 980 mg/kg. The process of lowering the toxicity is continuing. Of the compounds recommended for use at present, 30% are specific toxicants for which LD_{50} exceeds 1000 mg/kg (tetrachlorvinphos—1900-5000, dilor—5000-9000, menazon—1200-3300, tetradifon—500-10 000, phoxim—over 2000 mg/kg, and so on).

The toxicity of the recommended fungicides and seed protectants has also lowered considerably. The average toxicity of fungicides in 1970 was 1000-3000 mg/kg, while in 1979 it was 10 000 mg/kg. Up to 1970, most seed protectants were characterized by an average toxicity of 25-30 mg/kg, whereas in 1979 this parameter for the main body of protectants exceeded 1000 mg/kg. The use of mercury formulations is restricted; less dangerous, but no less effective substances can be used instead of them (Yu. Fadeev *et al*, 1981).

Chemical means of plant protection occupy the leading place as regards their total volume of application in the general system of integrated management of pests and diseases of plants and of weeds. But in addition to their large merits, it is also necessary to note the shortcomings of pesticides, first of all their toxicity to humans and warm-blooded animals.

Some formulations from the group of organochlorine compounds, triazines, picolinic acid derivatives (picloram), and urea are distinguished by their increased persistence in biological media and decompose slowly in them. This creates a hazard of their accumulation in natural conditions. The frequent use of the same formulations leads to the appearance of resistant races of insects that are no longer affected by these pesticides. In addition, owing to their universal

nature, chemical means eradicate both harmful and beneficial insects, which results in violation of the biocoenoses and the killing of birds, predatory and parasitic insects, bees, etc. This is why further improvement of chemical plant protection means is necessary to eliminate the possible unfavourable consequences with respect to the environment. Chemical plant protection means must meet the following requirements: a low acute and chronic toxicity to humans and animals; a moderate persistence and the ability to decompose during one vegetation period in the environment; a high technical and economical effectiveness, convenience in use, storage, and transportation, and selectivity with respect to beneficial organisms. It is necessary to work out systems of alternation of insecticides relating to different classes of chemical compounds with different mechanisms of action on the harmful organisms, to create more effective insecticides for controlling soil-dwelling pests, new systemic fungicides, and also herbicides for controlling weeds resistant to 2,4-D. Awaiting its solution is the problem of the joint use of insecticides and attractants for exterminating harmful insects on bait plots, which excludes overall treatments.

The ways and means of pesticide application must be improved to diminish the losses of the active ingredients and reduce their rates of use. An important problem is the improvement of the methods of chemical analysis of microamounts of pesticides in food products, fodder, the soil, water, and the atmospheric air.

Chemical plant protection is a science dealing with pesticides, their physicochemical and toxicological properties, their effect on harmful organisms and elements of the environment, and also with the proper use of pesticides in a system of integrated pest management. The main task of the course in chemical plant protection is training in the proper use of modern chemical means, studying of their nature and mechanism of action, and of the most rational and safe ways of using pesticides.

The theoretical cornerstone of chemical plant protection is agronomical toxicology—the science dealing with the poisons used in agriculture.

A theoretical task of the course in chemical plant protection is the studying of the physiological action of various chemicals on harmful organisms and cultivated plants in order to find the best ways of protecting agricultural crops from harmful organisms.

Since all chemical means of plant protection are toxic to humans and warm-blooded animals, the course treats at length measures of personal and public safety in working with pesticides.

The proper and safe use of pesticides will be ensured by a good knowledge of their physicochemical properties, features of application, and a knowledge of their toxicological characteristics and behaviour in biological media.

General Part

Chapter 1

CLASSIFICATION OF CHEMICAL MEANS FOR PLANT PROTECTION

The chemical compounds used to control pests and diseases of plants, to eradicate weeds, to kill pests and microorganisms that spoil agricultural products, materials, and articles, and to control parasites and vectors of dangerous diseases of man and animals are called **pesticides.**

The latter are classified according to their chemical composition, their targets, and also according to the ways they penetrate into an organism and the nature of their action.

With respect to their chemical composition, three main groups of pesticides are distinguished.

1. Inorganic compounds (compounds of mercury, fluorine, barium, sulphur, copper, and also chlorates and borates).

2. Pesticides of a vegetative, bacterial, and fungal origin (pyrethrins, bacterial and fungal preparations, antibiotics, and phytocides).

3. Organic compounds. This is the most extensive group including pesticides having a high physiological activity:

organochlorine compounds (hexachlorocyclohexane, polychloropinene, toxaphene, heptachlor, endosulfan, dilor, etc.)*;

organophosphorus compounds (dichlorvos, tetrachlorvinfos, trichlorfon, parathion-methyl, fenitrothion, trichloromentafos-3, bromophos, metasystox, malathion, phenthoate, phosmet, phosalone, dimethoate, formothion, etc.

derivatives of carbamic, thio- and dithiocarbamic acids (carbaryl, pirimicarb, chlorpropham, barban, phenmedipham, EPTC, pebulate, zineb, metiram, thiram, etc.

nitroderivatives of phenols (DNOC, dinobuton, nitrafen, dinocap, binapacryl);

phthalimides (captan, folpet);

mineral oils;

organic mercury compounds (ethylmercury chloride, mercurhexan, etc.);

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* A detailed description of each of the pesticides listed here, including its active chemical ingredient and its main properties, is given in the Special Part—*Translator's note.*

quinones (dichlone);
carbamide derivatives;
1,3,5 triazines, etc.

With respect to what they are used to control, all chemical formulations (pesticides) are divided into the following groups:

insecticides—for protecting plants from harmful insects;

acaricides (*acarus*—mite)—for protecting plants from harmful mites;

insectoacaricides—for simultaneously protecting plants from harmful insects and mites;

ovicides (*ovum*—egg)—for destroying the eggs of harmful insects and mites;

larvicides—for destroying the larvae of insects and mites;

molluscicides—for protecting plants from mollusks;

nematicides (nematodes—round worms, phytohelminths)—for protecting plants from harmful nematodes;

rodenticides—for controlling harmful rodents;

fungicides—for protecting plants from fungal diseases;

bactericides*—for protecting plants from bacterial diseases;

herbicides—for destroying grassy (weedy, poisonous) vegetation;

arboricides—for destroying trees and shrubs;

algicides—for destroying algae.

This classification is provisional to a certain extent because many pesticides have universal action and kill larvae and mites in addition to insects. For example, fenitrothion and malathion are both insecticides and acaricides, and for this reason the term **insectoacaricides** is applied to them; many pesticides control fungal diseases, as well as harmful insects and mites (for instance, DNOC, dinocap, binapacryl, and sulphur formulations), and the term **acarofungicides** is used for them.

Many herbicides when their dose is increased can destroy trees and shrubs, i.e. belong to arboricides.

With respect to the ways they penetrate into an organism and the nature of their action, pesticides are divided into stomach, contact formulations and fumigants. This classification makes it possible

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* This group of pesticides includes a large number of chemicals used to treat seeds, as antiseptics, for the treatment of plants and disinfecting the soil.

to judge how the poisons penetrate into an organism and, consequently, how they are used.

Stomach insecticides poison harmful insects when they enter their organism together with food.

Contact insecticides kill insects upon contact with the integument.

Fumigants are chemical substances that penetrate into the organisms of insects and animals through the respiratory tract in the form of a gas or a vapour. They also include insectoacaricides having a fumigant action that poison harmful insects and mites when they enter their organisms through the respiratory tract.

This classification is also provisional to a certain extent because many pesticides have a stomach, contact, and fumigant action. Examples are hexachlorocyclohexane (HCH) and heptachlor.

All pesticides are also divided into two large groups—with contact and systemic action. The former include chemical substances that kill or suppress harmful organisms upon contact with them. Pesticides with systemic action include chemical substances capable of penetrating into plants, moving in their tissues, and of causing the harmful organism (a weed, pathogen, pest) to perish as a result of feeding.

Herbicides with respect to the nature of their action are divided into selective and contact ones.

At present, investigations are being conducted for studying, separating, and using many biologically active substances in the protection of plants. The following groups of these substances are distinguished.

Pheromones—substances produced by insects and excreted into the surrounding medium for acting on other specimens.

Attractants—substances whose odour and taste attract insects and animals.

Repellents—substances whose odour and taste repel insects.

Inhibitors—organic or inorganic substances of a varied chemical nature, and also the products of metabolism of a cell that cause the partial or complete suppression of the activity of enzymes or metabolism in a living organism.

Sterilants—various chemical substances that when introduced into an organism deprive it of the ability of reproduction.

Hormones—substances with a very high biological activity that are secreted into the internal medium of an organism and control its most important functions (in insects—their metamorphosis).

Antifeedants—substances suppressing the feeding of insects.

Among the pesticides used in the chemical protection of plants, substances having a specific action are earmarked:

defoliants—substances causing the leaves of plants to fall off;

desiccants—substances accelerating the drying of standing plants;

retardants—substances retarding the rates of growth of plants, which results in their having shorter stalks and shoots.

All pesticides produced by Soviet chemical enterprises must comply with the requirements of the relevant state standards as regards their quality indices, i.e. must be standard. The standards indicate the exact name of a formulation (chemical and common), its composition, the technical requirements for its manufacture, the content of the active ingredient and carriers, the moisture content, the fineness of grinding for dusts and wettable powders, the ways of taking samples for analysis, and the ways of analysing the content of the active ingredient. They also indicate the packing of the pesticide and the conditions for its storage. When working with a pesticide before approval of the relevant state standard, specifications approved by the Ministry of the Chemical Industry are used. They contain the main indices characterizing the given pesticide.

Every year, the State Board for Chemical Means of Controlling Pests, Plant Diseases, and Weeds under the USSR Ministry of Agriculture considers the results of pesticide tests and their use in production.

Subject to approval by the USSR Ministry of Health, the USSR Ministry of Agriculture approves the "List of Chemical and Biological Means of Controlling Pests, Plant Diseases, and Weeds" allowed to be used in agriculture during the forthcoming year.

Chapter 2

FUNDAMENTALS OF AGRICULTURAL TOXICOLOGY

Toxicology (*toxicum*—poison, *logia*—speech, word) is a science dealing with poisons and their action on organisms.

Agricultural toxicology is a branch of the science studying the properties of the pesticides used in agriculture, their action on warm-blooded animals, insects, bacteria, on fungi, plants, biocoenoses, and ecological systems.

The ability of pesticides to act on some living beings without harming others underlies their widespread use for protecting plants from being damaged by harmful organisms.

The main task of agricultural toxicology is to provide the theoretical cornerstone for the purposeful synthesis of pesticides and for developing effective ways of their application excluding the possibility of their adverse influence on humans and beneficial animals.

2.1. Poisons and Poisoning. The Toxicity of Pesticides

Poisons are substances which when they enter an organism in different ways (through the respiratory tract, integument, alimentary tract) in insignificant amounts are capable of causing malfunctioning of its vital activity which in definite conditions results in an unhealthy state, i.e. produce a toxic effect.

Many natural compounds, products of the vital activity of plants and microorganisms, and also artificially produced chemical substances are poisonous. Exogenic poisons that enter an organism from outside, and endogenic ones formed in an organism itself are distinguished.

The concept "poison" implies interaction between a living organism and a substance. A poison is always a chemical substance. Chemical substances taken separately or when reacting with substances of an inanimate nature cannot be poisons and become such only when they interact with an organism and cause pathological changes to appear in it. With a gradual diminishing of the amount of a poisonous substance acting on an organism, the pathological effect weakens or even vanishes completely. Consequently, the reaction of an organism and the manifestation of poisonous properties of chemical substances are determined by the amount of a substance interacting with the organism.

Toxicity is the property of a pesticide, when used in small amounts, to upset the normal vital activity of an organism and cause it to be poisoned, to perish. Acute and chronic poisoning are distinguished.

Acute poisoning of an organism by a pesticide occurs when the pesticide acts once. It manifests itself in upsetting of the vital activity of the organism with a possible lethal outcome. It is attended by rapid development of the ailment.

Chronic poisoning of an organism is the result of the repeated action of relatively small amounts of a pesticide and manifests itself in slowly developing malfunctioning of normal vital activity.

The toxicity of pesticides varies and depends on their amount, the ways of entrance, the duration of action, the state of the organism, the environment, etc.

A measure of the toxicity of pesticides for various organisms is the **dose**—the amount of a pesticide causing a definite effect. The dose is expressed in units of mass of the pesticide per unit of area, volume, or mass of the object being treated.

The organisms used for determining the toxicity are called **biotests,** and the individual indices showing the change in the biochemical and physiological processes used to determine the degree of poisoning are called **tests.**

The effect of the action of pesticides on the organisms being studied is determined according to their extermination or according to the most characteristic features of poisoning (a change in the activity of individual systems of the organism, its reaction, lowering of the reproducibility, mass, growth, etc.) and is expressed as a percentage relative to the reference organisms.

The experimentally established optimal amount of a pesticide or working composition recommended for the protection of plants in field conditions and evaluated to obtain a high economical effect is called the **rate of use.** It is expressed in grams, kilograms, or litres of pesticide used per unit of area being treated (m^2, ha), or per unit of mass or volume of the product being treated (kg, tonne, m^3).

The **concentration** of the working solutions is also established for pesticides. It is expressed in per cent by weight or volume.

The toxicity indices are designated by the following symbols: LD (lethal dose), LC (lethal concentration), and ED (effective dose), with indication of the effect.

If the effect of the action of a pesticide is evaluated according to the number of perished objects, the indices LD and LC are used. For example, LD_{90} is the dose of a pesticide that resulted in the perishing of 90% of the specimens; LC_{20} is the concentration of a pesticide that resulted in the perishing of 20% of the specimens. If the effect of the action of a pesticide is evaluated according to the degree of violation of separate vital activity processes (the accumulation of dry matter, inhibition of growth, the onset of separate reactions, and so on), ED is the quantitative index.

The degree of toxicity of a substance is characterized by the threshold, toxic sublethal, and toxic lethal doses or concentrations.

The **threshold dose** is the smallest amount of a substance causing changes in an organism that are determined by the most sensitive biochemical and physiological tests in the absence of external indications of poisoning of an animal.

A **toxic sublethal dose** causes visible manifestations of poisoning of an organism without a lethal outcome.

A **toxic lethal dose** causes poisoning of an organism terminating in its perishing.

It is impossible to accurately establish the dose of a pesticide causing a definite effect on an individually taken animal, insect, or plant because biological objects are characterized by a varying individual sensitivity to pesticides. For this reason, toxicity is assessed in practice according to an averaged characteristic, most often according to the dose producing a 50% effect—the **median lethal dose**.

The quantitative indices of pesticide toxicity are determined experimentally. For this purpose, groups are separated from among the objects being studied, and they are treated with different (often logarithmically increasing) doses of the relevant pesticide. The effect is determined after time has elapsed sufficient for the optimal manifestation of the effect of the pesticide. The effect is expressed as a percentage of the reference (without a pesticide) variant with account taken of the most characteristic changes in an organism caused by the given pesticide. The result is a statistical series in which the effect grows with an increasing dose.

The data obtained are used to plot a graph of the effect against the pesticide dose. Experimental data show that the dependence of the effect (in per cent) on the dose is expressed by an asymmetrical S-shaped curve because increasing doses of a pesticide produce, as a rule, a gradually attenuating effect. This makes it difficult to determine the required dose from such a graph. If we take the logarithms of the doses instead of their absolute values to plot the graph, the curve becomes a symmetrical S-shaped one and at the middle values of the effect it approaches a straight line. But at doses causing effects close to 0 or 100%, the relation differs appreciably from a linear one.

To straighten this line, the method of probit analysis is used. The procedure is to convert the effect percentages into conditional probability units called **probits** (*prob*ability + un*its*). The values of the probits corresponding to a given effect percentage are found in special tables (Table 1).

When plotting the values of the probits and the dose logarithms, random deflections of individual points from a straight line may occur. A linear dependence of the effect on the dose is plotted on the basis of a solution of the correlation coupling equation, or empirically, and the resulting graph is used to find LD_{50}, ED_{50}, or other required indices (LD_{16}, ED_{84}, etc.).

The toxicity indices help us determine the rates of use of a pesticide and the more effective ways of applying it. The lower the absolute value of an index, the higher is the toxicity characterizing a formulation. A comparison of LD_{50} of the same pesticide for various objects gives its selectivity. For instance, if for a culture ED_{50} of a herbicide is 8 mg per kg of soil, and for the most widespread weeds it is 0.2 mg/kg, the herbicide has a high selectivity.

Table 1. Conversion of Percentage to Probits

Percentage perished	Probit	Percentage perished	Probit
1	2.674	51	5.025
2	2.946	52	5.050
3	3.119	53	5.075
4	3.249	54	5.100
5	3.355	55	5.126
6	3.445	56	5.151
7	3.524	57	5.176
8	3.595	58	5.202
9	3.659	59	5.227
10	3.718	60	5.253
11	3.773	61	5.279
12	3.825	62	5.305
13	3.874	63	5.332
14	3.920	64	5.358
15	3.964	65	5.385
16	4.006	66	5.413
17	4.046	67	5.440
18	4.085	68	5.468
19	4.122	69	5.496
20	4.159	70	5.524
21	4.194	71	5.553
22	4.228	72	5.583
23	4.261	73	5.613
24	4.294	74	5.643
25	4.326	75	5.674
26	4.357	76	5.706
27	4.387	77	5.739
28	4.417	78	5.772
29	4.447	79	5.806
30	4.476	80	5.842
31	4.504	81	5.878
32	4.532	82	5.915
33	4.560	83	5.954
34	4.587	84	5.994
35	4.615	85	6.036
36	4.642	86	6.080
37	4.668	87	6.126
38	4.695	88	6.175
39	4.721	89	6.227
40	4.747	90	6.282
41	4.772	91	6.341
42	4.798	92	6.405
43	4.824	93	6.476
44	4.849	94	6.555
45	4.874	95	6.645
46	4.900	96	6.751
47	4.925	97	6.881
48	4.950	98	7.054
49	4.975	99	7.326
50	5.000	99.99	8.719

The quantitative indices of toxicity are of a great significance for establishing the appearance of the resistance of insects to pesticides. For example, to assess the change in the resistance level of a population of mites being treated, it is necessary to know the initial sensitivity of the mites and in the course of treatments to compare it with the acquired resistance.

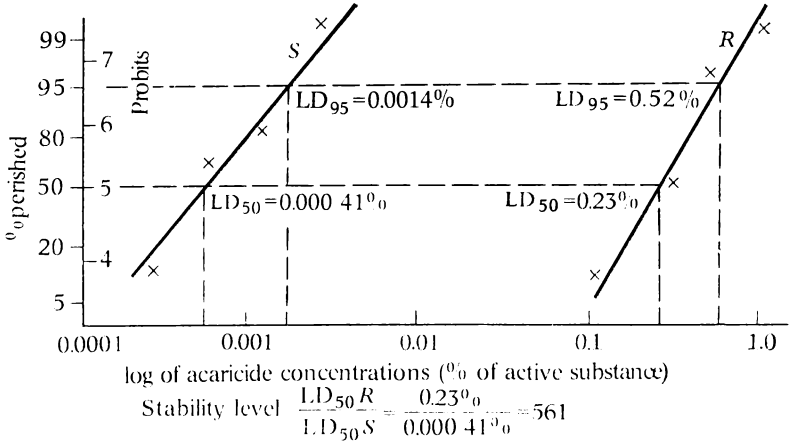

Fig. 1. Perishing of mites of various populations versus acaricide doses: S = curve for sensitive population; R = curve for resistant population

Figure 1 shows how the extermination of mites of a sensitive (S) and a resistant (R) populations depends on the acaricide doses. The resistance level is characterized by the ratio of LD_{50} for the sensitive (not treated by the pesticide) population to LD_{50} for the population whose resistance is being studied. The data obtained show a growth in the initial value of LD_{50} of 561 times. This indicates that the population of mites has acquired a high resistance at which it is not expedient to use the given acaricide*.

The dependence of the toxicity of a pesticide on its dose underlies the quantitative determination of pesticides in various media. The effect of pesticide action is determined, and then a graph of effect versus dose is used to find its amount. Unlike physicochemical methods of analysis, this method has been named **biological**.

The toxicity indices are also used for a hygienic characteristic of pesticides.

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* *Metodicheskie ukazaniya po ratsional'nomu ispol'zovaniyu sovremennykh akaritsidov v bor'be s rezistentnymi populyatsiyami pautinnogo kleshcha* (Methodical Instructions for the Rational Use of Modern Acaricides in Controlling Resistant Populations of Spider Mite). Moscow, Kolos (1977).

2.2. Penetration of Poisonous Substances into a Cell. Action on Enzymes

The cells of plants have a dense wall consisting of cellulose and other compounds.

The wall of a cell is pierced by plasmodesmi and has a high permeability to mineral and organic substances. When the compounds being absorbed pass through the walls of vegetative cells, they interact with the substances of the cell wall. This interaction may have the nature of molecular adsorption, ion exchange, or of combination with the components of the cell wall by means of stronger bonds. The substance is concentrated on the inner surface of the wall. Ions whose bond to the cell wall is unstable are easily desorbed into the free space of the cells and are absorbed by the cytoplasma. A second structural barrier in the way of substances being absorbed is a surface membrane. Biological membranes are intricate highly specialized formations surrounding a living cell and individual intracellular formations (organelles). They are mainly built up of lipids and proteins.

Biological membranes are barriers separating the contents of a cell from the environment. They also play the role of separating partitions between sections of a cell. Various substances and ions needed for the vital activity of a cell are carried through the membranes. This process is of a selective nature. Here we distinguish passive transmission, when the flow of substances occurs in accordance with the gradient of concentrations or electrochemical potentials, and active transmission at the expense of the energy generated in the cell.

The system of active transmission through biological membranes is exceedingly involved. In active transmission, the first step of absorption is the interaction of the substances being absorbed with the molecules of the surface structures of the cytoplasma. The adsorbed molecules are then carried over into the cytoplasma by means of the active transmission mechanism. It is presumed that the leading role in these processes is played by special transport systems—membrane carriers. One of the links in this system may be membrane transport adenosinetriphosphatases activated by magnesium, potassium, and sodium ions.

The penetration of pesticides into the cells of living organisms obeys the general laws. They may diffuse through membranes together with solvents along the gradient of concentrations. Lipophylic pesticides penetrate by dissolving in the lipid layer of a membrane. Pesticides also penetrate into cells by active translocation using the energy of high-energy compounds.

Most pesticides belong to highly active organic compounds. In the form of emulsifiable concentrates, they are lipophylic compounds.

For this reason, they readily dissolve in the lipids of the cell membranes and easily diffuse into the cells.

Mineral pesticides penetrate into a cell in the form of ions or undissociated molecules. The higher the solubility of a pesticide, the more rapidly and easily does it penetrate into cells. High-molecular compounds most probably enter the cytoplasma by pinocytose.

Upon penetrating into a living cell, pesticides change the physicochemical properties of the cytoplasma, destroy the membranes of the organelles, change the reaction of the medium (the pH), and disarrange the conditions of normal functioning of the cell proteins.

Enzymes—the biocatalysts of cells—are especially sensitive to the poisoning action of pesticides. The poisoning of an enzyme participating in an important metabolic process has a depressing, and sometimes a lethal action on an organism.

The inactivation of a definite key enzyme is known as **biochemical lesion.**

All enzymes are proteins and depending on the intricacy of their structure are divided into two classes: one-component and two-component enzymes. The former consist only of a protein having catalytic properties. The latter, in addition to a protein, include a non-protein part called a prosthetic group. The active prosthetic group is called an **agon** or **coenzyme**, and the protein part is called a **pheron**. Pesticides can interact either with the protein part of an enzyme molecule and completely inactivate it, or with the coenzyme and form stable compounds or unstable complexes. In both cases, the pesticides are enzyme inhibitors. The inactivation of enzymes by pesticides may be reversible or irreversible.

All enzyme inhibitors, including pesticides, can be conventionally divided into two groups—general and specific.

General inhibitors include salts of heavy metals (silver, copper, mercury, lead, tungsten), and also trichloroacetic acid and tannin that are protein precipitants and therefore suppress the action of all enzymes. Some enzymes are sensitive to low concentrations of these metals, for example, p-fructofuranosidase is inactivated by a saturated solution of AgCl.

The inhibition of enzymes by heavy metals is reversible upon the addition of substances forming complexes with the metals, for instance cyanide or ethylene diamidetetraacetate.

Specific inhibitors include cyanide, H_2S, sulphide, azide, and carbon monoxide acting on metals.

Cyanides form stable complexes with the metals in the composition of enzymes and inactivate them. For example, cyanides, H_2S, sulphides, and azide combine with iron and suppress the activity of cytochromes and, therefore, respiration. For this reason, they

have been named **respiratory poisons**. These substances suppress the action of many enzymes containing iron and copper in their active group.

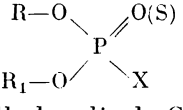
An especially active inhibitor is cyanide that suppresses many enzymes and acts on them in a very low concentration. For instance, cytochromoxidase is suppressed by 80% by cyanide in a concentration of 10^{-8} mol, cytochromperoxidase—by 50% in a concentration of 10^{-4} mol. Catalase is suppressed by 50% in a concentration of 5×10^{-6}, and peroxidase in a concentration of 10^{-5}. The action of cyanide exhibits itself in different ways: it combines with a metal and inactivates the active group of the enzyme; it combines with the carbonyl group in the enzyme, in the cofactor, or in the substrate; as a reducing agent, it can break the disulphide bonds underlying the activity of an enzyme. Carbon monoxide suppresses the activity of only the enzymes that are activated by iron and copper. This is why it inhibits a smaller amount of enzymes than cyanide.

Compounds containing arsenic and mercury act on the sulphhydril groups of enzymes.

Plants, animals, and bacteria have enzymes whose composition includes compounds containing sulphhydril groups such as cysteine and glutathione. Arsenic combines with the sulphur to form stable compounds, thus inactivating the enzyme. The enzymes oxidase, pyrophosphatase, and hexokinase are inactivated by compounds of arsenic and mercury. Consequently, the indicated compounds are toxic to all organisms because they contain all the named enzymes.

Organophosphorus inhibitors suppress the action of enzymes that catalyze the hydrolysis of esters. They suppress especially strongly the activity of cholinesterase and acetylcholinesterase that activate the decomposition of acetylcholine into choline and acetic acid. Cholinesterase is contained in nerve tissues and participates in the transmission of nerve pulses. This is why organophosphorus inhibitors are called nerve poisons.

Organophosphorus enzyme inhibitors also suppress the activity of chymotrypsin, trypsin, thrombin, plasmin, acetylesterase, carboxyethylesterase, and some lipases. Hence, not only esterase, but also proteolytic activity is suppressed. The general formula of organophosphorus inhibitors is



where R and R_1 are the alkyl radicals CH_3, C_2H_5, *iso*-C_3H_7 and X is F, CN, $OC_6H_4NO_2$, etc.

The organophosphorus inhibitors include a large number of modern insecticides and acaricides that are widely used in agriculture.

Notwithstanding the very high activity of organophosphorus inhibitors and the high stability of enzyme suppression by them, reactivation of the enzymes is possible when treated with definite oximes or hydroxamic acids. This treatment results in removal of the phosphoryl group because the process of inactivation of the enzymes is associated with their phosphorylation. This principle underlies the use of antidotes for preventing poisoning by organophosphorus compounds.

2.3. Metabolism of Poisons in an Organism

The entry of a poisonous substance into an organism calls forth responding protective reactions that restrict the toxic action of the poison. These reactions include excretion of the foreign substance from the organism in an unchanged form, deposition of it in the tissues, and decomposition of the poison into simpler substances with the following excretion thereof or inclusion into the general processes of metabolism.

Most pesticides are lipophylic substances, and this is why their excretion from the organism in an unchanged form occurs quite rarely. This is inherent in generally stable chemical compounds such as organochlorine insecticides. Only some hydrophylic compounds can be excreted from insect organisms through their system of Malpighian tubes, and in mammals through the kidneys with the urine. Cases of the excretion of toxic substances in an unchanged form are also known in plants. For instance, in jimsonweed datura, during the first day after applying 2,4-D to a leaf, up to 60% of the entire herbicide applied is excreted through the roots into the nutrient solution. A poison may be discharged from the organism or an insect or mammal together with the excrements, especially with undigested substances, and in the course of vomiting, when the toxic agent greatly irritates the mucous membrane of the alimentary tract.

Finally, an important process inherent only in mammals is the excretion of pesticides from an organism together with milk. Stable organic substances, for instance certain organochlorine compounds, can be excreted in this way.

The deposition of a toxic substance is a property of all living organisms and leads to temporary localization of the poison in tissues that do not participate actively in vitally important processes.

Upon penetrating into the organism of an insect, an insecticide dissolved in lipids may accumulate in the fat-body and render no toxic action. The deposited substance is then decomposed and is excreted through the Malpighian tubes or is removed in molting together with the chitinous shell. In the organism of an animal, the deposition of poisonous substances occurs in the fat cells,

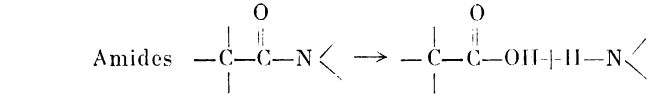
while some compounds combine with the serum albumin of the blood. Both these processes precede the decomposition of the toxicants.

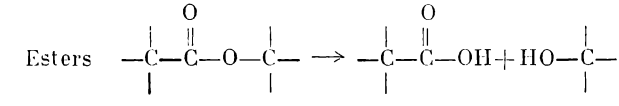
The most widespread reaction of any organism to the introduction of a foreign substance is its decomposition. As a result, either less toxic (detoxication) or more poisonous (activation) products may be formed. The most stable are the halogen derivatives of the cyclic hydrocarbons and heterocyclic compounds, while the esters of phosphoric acid are less resistant. In the long run, metabolism results in more simple and hydrophylic substances that are easily excreted from the organism or are utilized in the general processes of metabolism.

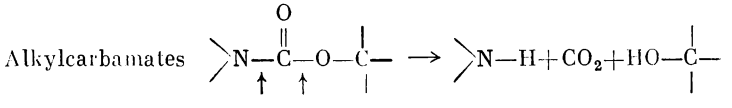
Several basic types of reactions occurring in an organism are known. They include hydrolysis, oxidation, reduction, dehydrochlorination, isomerization, and conjugation. These reactions are catalyzed by enzymes, and many of them also require a hydrogen donor.

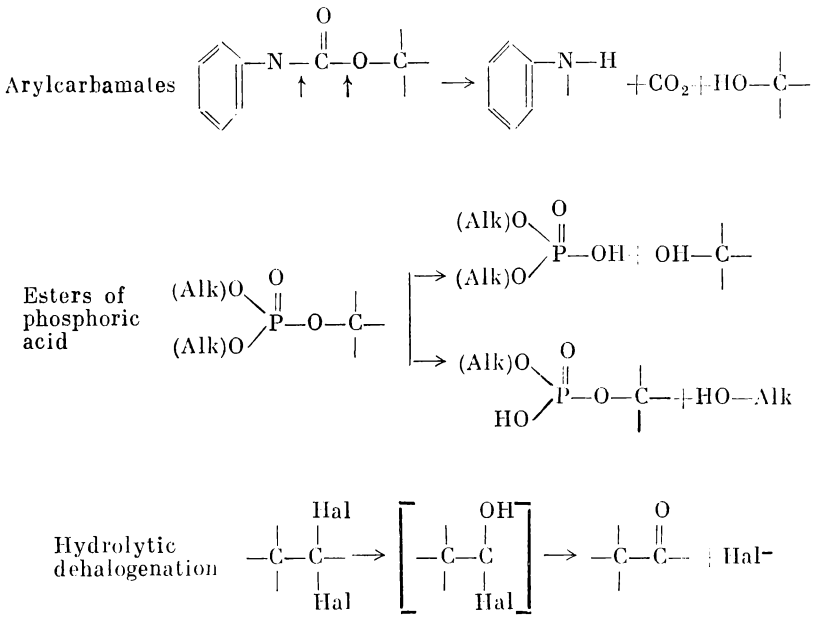
The hydrolysis of poisons in organisms may occur either chemically or with the aid of enzymes. The main role in this process is played by enzymes such as amidase, nitrilase, phosphatase, and carboxyesterase whose activity in living organisms is quite high.

Hydrolytic decomposition is characteristic of pesticides of the amide group (propanil), esters of various acids (esters of 2,4-D and MCPA), alkylcarbamates (carbaryl), arylcarbamates (barban), organophosphorus compounds (parathion-methyl), and halogen derivatives of hydrocarbons (hexachlorobutadiene). The products are acids on the one hand and alcohols or amines on the other. Aryl- and alkylcarbamates are a special case because the acids formed in their hydrolysis are very unstable and rapidly decompose into CO_2 and the corresponding amines.









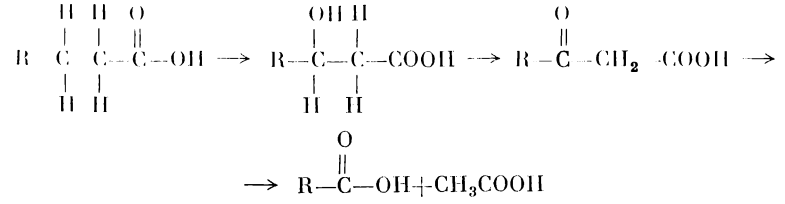
In hydrolysis, lipophylic substances transform into hydrophylic ones, and the nature of the behaviour of poisons in an organism sharply changes. The reaction products penetrate only slightly through the membranes to the vitally important centres and are excreted from the organism at a faster rate.

In the majority of cases, hydrolysis results in the formation of substances that are less toxic to organisms. There are poisons, however, whose toxicity increases after hydrolytic decomposition. For instance, acetyldipterex hydrolyzes under the influence of enzymes to trichlorfon, the latter being more toxic to insects and animals.

Oxidation is one of the widespread types of metabolism of poisons in an organism. The mechanism of these reactions is often quite involved, and their proceeding requires enzymes and coenzymes, as well as hydrogen donors. For many substances that resist hydrolysis, oxidation is the main direction of metabolism in organisms. The substances formed may have a higher or a lower toxicity, and a low or high resistance to hydrolysis.

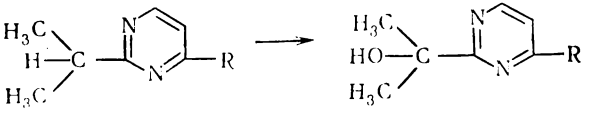
Various fatty acids and their derivatives that get into a living organism are decomposed by means of the beta-oxidation mechanism. It consists in the stepwise decomposition of fragments of the hydrocarbon chain with an even number of carbon atoms to acetic

acid:

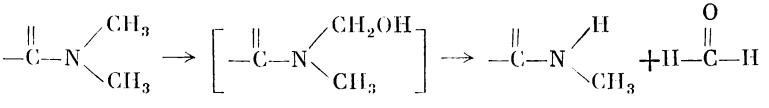


This process is of special significance for phenoxycarboxylic acid derivatives. Phenoxybutyric acids, having a low physiological activity, can be oxidized in plants to the corresponding phenoxyacetic acids characterized by a higher phytotoxicity. Depending on the activity of the beta-oxidation systems, the sensitivity of plants to herbicides varies.

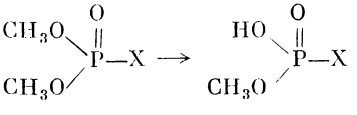
The oxidation of the side bonds of cyclic and heterocyclic compounds often occurs when direct hydroxylation of the ring is hampered. More polar and less toxic products are formed, and at the same time ring decomposition processes are accelerated:



Examples of non-specific oxidation reactions are the reactions of N- and O-dealkylation that are catalyzed by various oxygenases and require a hydrogen donor such as $(NADPH)H_2$. These reactions are the main non-hydrolytic way of decomposing certain pesticides in biological media, especially alkylamines, alkylamides, alkylcarbamates, and derivatives of alkyl urea:

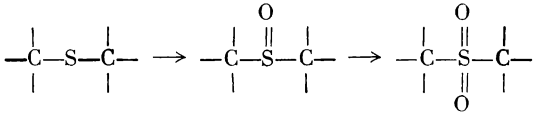


O-dealkylation plays a significant role in the process of decomposing pesticides of phosphoric and phosphonic acid derivatives, and also of other substances containing an alkoxy group, sharply increasing the hydrophilic properties of the metabolites:

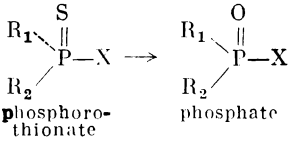


Of great importance in the metabolism of pesticides are the reactions of oxidation of the sulphur atom in the molecules of some sub-

stances. This is characteristic of insecticides from the group of derivatives of carbamic and phosphoric acids. The thioester sulphur in these compounds is oxidized regardless of the structure of the remaining part of the molecule. The corresponding sulphoxide is first formed, and then a sulphone:



The oxidation products do not differ in their toxicity from the initial substance, but are considerably more stable to hydrolysis. These reactions occurring in plants underlie the prolonged insecticidal action of a number of esters of phosphoric acids with a thioester radical. The oxidation of phosphorothionates in various organisms is considered as an activating step in the process of metabolism of these substances:

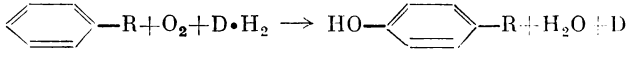


where X is an acid residue, and R_1 and R_2 are hydrocarbon radicals.

The toxicity of the reaction product to mammals and insects increases scores and hundreds of times in comparison with the initial substance. These toxic metabolites, however, are readily hydrolyzed and therefore remain for only a short time in biological media.

Oxidation reactions are of great significance in the process of decomposition of the aromatic ring and the metabolism of stable pesticides, for instance, the halogen derivatives of hydrocarbons. Cyclodiene compounds (heptachlor) are distinguished by the direct oxidation of the double bonds with the formation of epoxides that are more toxic than the initial substances and are the first metabolites from which decomposition of a pesticide in organisms begins.

The hydroxylation of the aromatic ring in the molecules of many poisons is a prerequisite for its further decomposition and occurs with the participation of a hydrogen donor. A polar group is introduced into a molecule of the poison, and as a result the polarity of the molecule grows with a corresponding decrease in the toxicity of the compound:



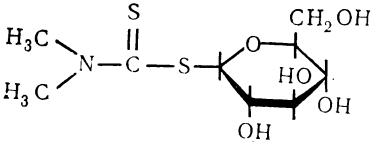
Among the other reactions leading to a loss of toxicity of a poison in an organism, we must note the reduction of the nitrogroup and

dehydrochlorination. The former is characteristic of substances having a nitrogroup at the benzene ring (parathion-methyl) and leads to the formation of the corresponding aminoderivatives having a lower physiological activity.

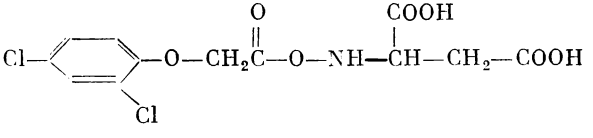
Dehydrochlorination (detachment of hydrogen chloride molecules) is a feature of chlorinated hydrocarbons and certain other pesticides and proceeds in an alkaline medium or with the participation of enzymes. This reaction may result in the formation of products having either a higher or a lower toxicity than the initial one.

Conjugation reactions are processes of biosynthesis in which substances that are foreign to an organism combine with endogenic chemical compounds. The complexes (conjugates) that are formed are, as a rule, more polar, mobile, and less toxic. Among such reactions are acetylation, the formation of sulphates, conjugation with amino acids, glucose, and glutathione, and O- and S-methylation. They occur first of all in pesticides containing phenol, heterocyclic, and other cyclic groups in their molecules. The conjugation process involves both the pesticides themselves and the products of their metabolism (alcohols, phenols, carboxylic acids, amines, thioles, heterocyclic and cyclic compounds). Depending on the biochemical features of the processes in an organism, the type of prevailing reaction varies: in vegetative organisms the formation of glycosides and glycosoamines is encountered most often; in the organisms of insects—of sulphates, conjugates with amino acids, glutathione, and glucose; in the organisms of warm-blooded animals—conjugates with glucuronic acid, amino acids, sulphuric acid, and glutathione.

For instance, when derivatives of dithiocarbamic acid penetrate into plants, they form conjugates with glucose:

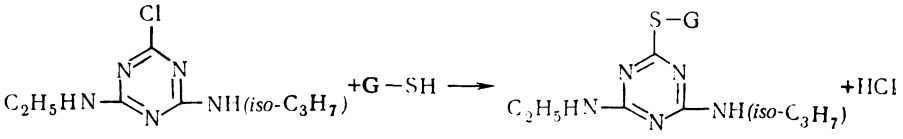


while 2,4-D also forms conjugates with amino acids:

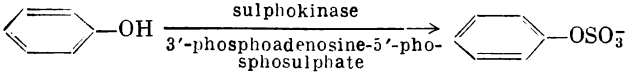


The conjugation of atrazine in an animal's organism with glutathione leads to detachment of Cl in the second position and to the

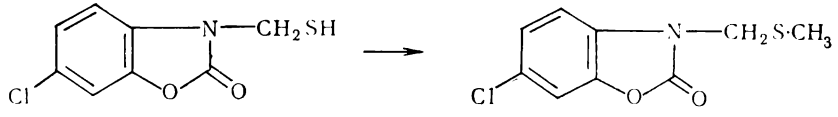
loss of toxicity:



An important path in the metabolism of phenols, alcohols, and aromatic amines is the formation of sulphates:



When phosalone is decomposed in the organism of animals, S-methylation of a heterocycle is of great significance as a reaction of detoxication of biologically active metabolites:



The process of transformation of a poison in an organism does not go on in one strictly definite way. On the contrary, the same compound may be involved in different reactions, as a result of which a variety of exchange products is formed. Some of the reactions lead to activation of the poison, while others lead to its detoxication. The direction of these processes depends on the specific and individual features of an organism and to a considerable extent determines the selectivity of pesticide action.

The processes of metabolism of poisonous substances when they penetrate into an insect's organism together with its food begin already in the front intestine under the action of the enzymes in the saliva and proceed actively in the middle intestine in either an enzymatic or a chemical way. The main reactions here are hydrolysis with the formation of polar and only slightly toxic products. When aromatic compounds are sucked into the middle intestine, they may be transformed into the relevant glycosides that are then excreted through the Malpighian tubes.

The toxic substances continue to be decomposed after being sucked in and getting into the hemolymph, while a part of these substances is rendered harmless in the fat-body.

When a poison penetrates into an insect's body through its integument, the processes of insecticide metabolism occur mainly in the fat-body whose enzymes are very active. Here oxidation, hydrolysis, reduction of the poison and its conjugation with other com-

pounds occur. The metabolites in this case may be excreted through the Malpighian tubes or deposited in the cells with the following separation when the insect moults.

In mammals, active hydrolytic decomposition of a poison occurs under the action of the enzymes in the saliva, the gastric juice, and the blood. But the main organ rendering poisonous substances harmless is the liver with its powerful enzyme apparatus. Pesticides and their decomposition products getting into the blood enter the liver, where they undergo processes of decomposition (hydrolysis, oxidation, reduction, etc.) and conjugation with the formation of water-soluble compounds. The latter are excreted from the organism via the kidneys with the urine or get together with the bile into the intestine, whence they are excreted together with the fecal matter. The products of decomposition of some pesticides may be discharged from the organism of warm-blooded animals in the gaseous form via their lungs. The fatty tissue of animals is also not absolutely inert. Pesticides deposited in it gradually decompose into only slightly toxic products, although the rate of this process is considerably lower than in the liver.

In plants, fungi, and bacteria, the processes of metabolism of poisonous substances go on more slowly than in animal organisms, and their rate depends greatly on the environmental conditions: in more favourable conditions a poison decomposes more intensively, and a plant overcomes its toxic action more rapidly. No special organs or tissues rendering poisonous substances harmless have been discovered in plants. Certain soil herbicides (atrazine) are known to decompose more rapidly in the roots of plants than in their leaves.

The products of pesticide transformation are mainly excreted from plants through their stoma in the form of CO_2, NH_3 and other gaseous substances, and with the root excretions. Many poisons and the products of their metabolism move along the vascular system in the form of conjugates with glucose, amino acids and some organic acids.

All the processes associated with the metabolism of poisons mainly occur in any organism in a cell. Here we can point out the main laws inherent in all organisms and explaining why the toxicity of poisonous substances is selective.

A common feature of all cells is the presence of an endoplasmic reticulum whose canals are connected to membranes, owing to which exchange is achieved between them. In addition, the endoplasmic reticulum is the place where the numerous enzymes responsible for reactions of oxidation, hydrolysis, reduction, and synthesis of many substances are concentrated. In experiments with liver homogenates of mammals and the fat-body of insects, it was established that it is exactly the enzymes of the endoplasmic reticulum that play the decisive role in the processes of metabolism of pesti-

cides. Regardless of the kind of reaction, the products of the enzymic transformations are always more polar and less lipid-soluble than the initial substances. This facilitates their excretion from the organism.

According to B. Brodie, such enzymes developed in the course of evolution as a means ensuring the more rapid excretion from an organism of admixtures to food such as alkaloids, terpenes, and steroids. Owing to their low specificity, individual enzymes of the endoplasmic network can decompose pesticides.

The activity of the enzymes of the endoplasmic reticulum may change under the influence of various physiologically active substances whose metabolism occurs with the participation of just these enzymes. This phenomenon was called **induction,** and the substances producing it—**inducing agents.** After the introduction of an inducing agent, there is observed an increase or a decrease in the rate of decomposition of one or more poisonous substances by the microsome fraction (sections of the endoplasmic network after separation with the aid of an ultracentrifuge) of a mammal's liver or an insect's fat-body. The induction effect was first established for medicines. It was subsequently found that many insecticides are induced agents. After treating the insects *Triatoma infestans* with small doses of organochlorine formulations, an increase was noted in the ability of the microsome fraction of the fat-body to decompose these insecticides into polar compounds that are readily excreted from the organism. Therefore, the resistance of the insect to these substances grows. Chlorinated hydrocarbons may also induce activation processes. For example, after being introduced into a rat's organism, the toxicity of heptachlor increases owing to activation of the process of formation of heptachlor epoxide.

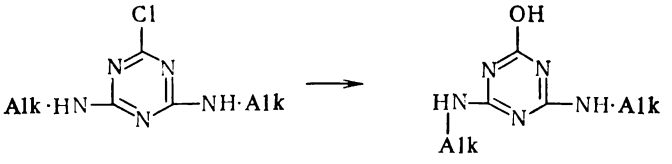
The phenomenon of induction explains the resistance of insects to insecticides. It is considered at present that the appearance of cross-resistance is due to the increase in the activity of the enzymes of the endoplasmic reticulum decomposing poisonous substances after the use of an insecticide.

2.4. Toxicity of Pesticides to Harmful Organisms and Factors Determining It

The main requirement which chemical means of plant protection must meet is their high toxicity to harmful organisms.

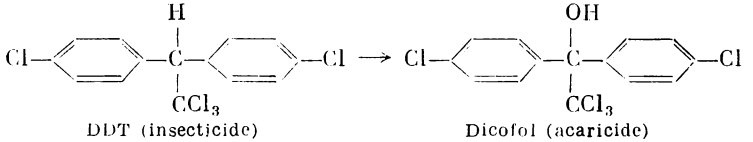
The toxicity of pesticides depends on the features of the chemical structure of the substance. Sometimes, even insignificant changes in the structure of a molecule lead either to the complete loss of toxicity or to a change in the spectrum of action. For example, substitution of the chlorine atom in the second position of the triazine ring in chlorine derivatives of 1,3,5-triazine (simazine, atrazine)

with hydroxyl results in a complete loss of the herbicidal activity:



Herbicides — Physiologically inactive substances

The introduction of the —OH group into a molecule of DDT leads to a sharp change in its spectrum of action. Instead of a very strong insecticide having no acaricidal activity, we obtain a substance (dicofol) that is highly toxic to herbivorous mites and only slightly toxic to insects:



DDT (insecticide) — Dicofol (acaricide)

Notwithstanding the considerable achievements in the field of the chemistry of pesticides, to date no general theory of how the pesticide properties depend on the chemical structure of a substance has been developed, although definite laws for separate classes of compounds have been established that allow the directed synthesis of pesticides with preset properties to be performed. Some of these laws will be treated when dealing with the properties of the relevant classes of pesticides.

The toxicity of various chemical compounds is sharply increased by introducing into their structure **toxophoric groups**—chemical radicals or atoms that increase the toxicity of a substance. Toxophoric groups include the halogens (Cl, Br, I, and F), the nitro group, atoms of the heavy metals (Hg, Sn, Cu), and the rhodanic group (—SCN).

For example, the halogen derivatives of hydrocarbons are considerably more toxic to insects, microorganisms, and plants than the corresponding parent compounds. Methyl bromide is a very effective fumigant and belongs to poisonous substances with a strong action, whereas the toxic properties of methane manifest themselves inadequately. When a nitro group is introduced into a phenol molecule, the insecticide activity grows sharply. If the lethal concentration LC_{50} of phenol for leguminous aphis is 0.3%, then LC_{50} for 4-nitrophenol is 0.007, and for 2,4-dinitrophenol is only 0.001%.

In a number of cases, the toxicity of substances increases when chemically inert methylene and methyl groups are introduced into

their molecules. For instance, diethyl phosphates are considerably more toxic than the corresponding dimethyl phosphates, which is evidently explained by the more rapid binding and decomposition of the latter in biological media. The insecticide activity of 2,4-dinitro-6-methylphenol is about double (LC_{50} for leguminous aphis is 0.0005%) that of 2,4-dinitrophenol.

The toxicity of chemical compounds often depends not on the composition of a substance, but on the structure of its molecule. Different isomers of the same substance have different activities.

The thiolo derivatives of thiophosphoric acid are several times more toxic to mammals than the thiono ones.

All the isomers of HCH (hexachlorocyclohexane) differ only in the spatial arrangement of the chlorine and hydrogen atoms. But only the gamma-isomer has insecticidal properties.

A knowledge of how the toxicity of organic compounds depends on their structure creates prerequisites for the synthesis of new highly effective pesticides.

We have already indicated that the toxicity of a poisonous substance is determined to a considerable extent by its dose.

The biological reaction of an organism (animal, insect, plant, fungus, etc.) acted upon by a poison is usually caused only by a small part of the total dose used in practice. This small amount of poison primarily blocks a vitally important function of the organism, after which secondary symptoms of poisoning develop that may lead to perishing of the entire organism. These considerations gave birth to the concept of the **target** (receptor). In accordance with our present notions of the mechanism of action of poisons, this target can be imagined as a specific tissue or organ, a definite type of cells or intracellular structure, and in the long run as a molecular receptor, for example a specific section of an enzyme or reaction. The toxicity of a substance will depend on how quickly and in what amount the poison penetrates to the target and enters into a reaction with it. This is why any factor affecting the processes of its reaction with the target causes a change in the toxicity.

The toxicity of a pesticide also depends on a number of factors without account of which its proper appraisal and use are impossible. These factors can be divided into three groups:

factors affecting the duration of contact of the pesticide with a harmful organism;

factors affecting the penetration of the pesticide into an organism;

factors associated with the behaviour of the toxic substance in an organism.

One of the factors affecting the toxicity of a pesticide is the **exposure** (the duration of contact of the poison with a harmful organism). The toxic action of a substance is known to grow with an increasing exposure because a larger amount of the poison enters the organism.

In the treatment of plants and the soil, the exposure depends directly on the **persistence** (duration of intactness) of the pesticide on the plants and in the soil. Of major significance here are the physicochemical properties of the pesticide and the environmental conditions.

Chemically stable substances with a low volatility persist for a long time on plants and in the soil. For this reason, it is preferable to protect plants by using pesticides that are highly toxic to the harmful organisms, are chemically stable, and have no other negative properties. For the better preservation of highly volatile substances, special antievaporators are introduced into the composition of formulations.

When highly volatile substances (EPTC, trifluralin, metam-sodium) are introduced into the soil, they are thoroughly covered or mulched, which improves the toxic action of the substances and prolongs their persistence in the soil.

Of great significance are properties of a pesticide such as adhesiveness and wettability, which prolong its persistence on the surface being treated and the contact of the substance with the harmful organism. To improve these properties, auxiliary substances—adhesives (stickers) and wetting agents—are added to pesticides.

Among the environmental conditions, the temperature renders the greatest influence on the toxicity of pesticides. A change in the temperature may lead to both a change in the activity of the substance itself and a change in the reaction of an organism. With elevation of the temperature, the losses of a pesticide from the treated surface increase, but this may be attended by a growth in the toxicity, for example as a result of the formation of more toxic substances (the transformation of thiono isomers of phosphorothioates to thiolo ones). At the same time, in conditions of the optimal temperature, an organism becomes more sensitive to the poison because the metabolism processes become more active. Pesticides whose toxicity increases with elevation of the temperature are related to substances with a positive temperature coefficient, while those whose toxicity decreases with elevation of the temperature—to substances with a negative temperature coefficient. Most modern pesticides belong to the first group. Only a few of them have a negative temperature coefficient, but their presence in the assortment of chemical means of plant protection is exceedingly important for managing pests in the early spring.

The duration of retaining the toxicity sharply diminishes under the action of humid air, solar radiation, winds, or precipitation. These factors indirectly lower the toxicity of a poisonous substance. In some cases, however, the toxicity of a pesticide may grow with an increase in the humidity, for instance upon the hydrolysis of calcium cyanide to the more poisonous hydrogen cyanide, or under

the action of solar radiation as a result of isomerization of thiono phosphates to thiolo ones.

All the soil factors affecting the persistence of pesticides in the soil will also influence their toxicity.

A poisonous substance upon contact with a harmful organism must rapidly and in a sufficient amount (a lethal dose) penetrate into the organism. This may occur in different ways (through the respiratory system, skin, and alimentary tract in the organism of an animal, through the epithelial tissues of fungi and bacteria, through the stomas and cuticles of the green organs and roots of plants), and this process is acted upon by a number of factors.

The unpleasant taste and sharp offensive odour of some pesticides prevent the good eating of poisoned food by their targets or prolonged contact of them with a treated surface, therefore an insect or animal does not receive a lethal dose of poison. For example, an insufficiently high effectiveness of antu may be due to the fact that owing to its bitter taste rodents eat poisoned bait poorly. The low toxicity of polychloropinene to the gray beet weevil is explained by the partly repellent properties of this insecticide. The pest avoids treated plants. This is why the production of pesticides with additions of attracting substances—attractants—is very promising. An example of such formulations is granulated metaldehyde with an addition of bran—a good feeding attractant for bare slugs.

The effectiveness of fumigants, rodenticides, and insecticides with stomach action depends to a large extent on the irritating property of the substance. Very strong irritation of the mucous membranes of the alimentary tract and the respiratory system results in vomiting and breathing spasmas. This leads to the poison together with food remnants being excreted from the organism, or to the entry of new portions of the poisonous substance being completely blocked. In the long run, an insignificant amount of the pesticide penetrates into the organism and does not render the required toxic action.

The toxicity of herbicides to plants may diminish as a result of the fact that the substance when it gets onto the leaves causes local burning of the tissues that prevents further penetration of the poison into the plant.

The epithelial tissues and shells of most organisms (for example, the cuticles of insects and plants) are poorly penetrated by aqueous solutions and other polar substances, whereas compounds soluble in lipids penetrate well through external integuments. In this connection, the toxicity of pesticides also depends on the solubility of the poison in lipids and the partition coefficient in the lipids-water system. It has been established that organic substances diffuse through the cuticle layers of insects and the skin of mammals in amounts proportional to their partition coefficients in the lipids-

water system. Consequently, the toxicity of pesticides to harmful organisms grows with an increase in their solubility in fats. Hence, the gamma-isomer of HCH (lindane), with a higher solubility in waxes, penetrates better into an insect's organism and is more toxic than the other isomers.

The solubility of pesticides in lipids, however, does not always clearly correlate with the toxicity. One of the factors violating this relation is the process of the dissolving of poisons in the lipids of the epithelial tissues with subsequent horizontal diffusion and loss because of evaporation and decomposition. Many organochlorine insecticides dissolve well in the waxes of the cuticles of insects and are retained in appreciable amounts in the upper layers of the epithelial tissues. A part of the pesticide migrates along the cuticle, evaporates, and decomposes into non-toxic products. Hence, the amount of poison entering an organism diminishes, and to achieve a toxic effect it is necessary to increase the dose of the formulation.

The penetration of poisonous substances depends to a great extent on the anatomical and morphological features of organisms. The entry of pesticides into organisms coated with a wax layer diminishes quite noticeably. Adult specimens of scale insects protected by a wax scale do not perish after treatment with aqueous suspensions or emulsions of organophosphorus insecticides that are toxic upon internal injection. The explanation is that aqueous solutions do not virtually penetrate under the scale of these insects.

The eggs of insects, the spores of fungi, and the cysts of nematodes are highly resistant to pesticides owing to the low permeability of their protective shells.

Many harmful organisms are capable of initiating special protective reactions preventing a toxic substance from entering them. Such reactions include: in stomach poisoning—freeing of the stomach and intestine from the poisoned food by vomiting or by inducing diarrhea; in poisoning by fumigants—isolation of the respiratory organs in insects by shutting their spiracles, and in the action of contact poisons—by excreting slime that glues the poison particles together and forms a specific casing around bare slugs; and autotomy (self-amputation of the limbs) in some insects. The result is a sharp decrease in the amount of poison entering the organism.

The toxicity of a poisonous substance is also noticeably affected by processes taking place inside an organism.

The toxicity of a poison to a given organism, in addition to other factors, depends on the rate of passive or active diffusion of the substances through various tissues. The higher the rate of penetration, the greater is the toxicity of a compound because the possibility of its being deposited and detoxified diminishes. Many organisms have internal structural barriers that prevent the penetration of poisonous substances to the vitally important centres. For example,

ionized organophosphorus compounds have a low toxicity to insects because they penetrate poorly through the shells of the nerve cord. In the organism of a mammal, the hemato-encephalic barrier (the membrane bedding the capillaries of the brain blood vessels) prevents the penetration of various poisonous substances into the brain. For this reason, the toxicity of pesticides depends on their ability to surmount such barriers.

A poison upon entering an organism may react not only with a vitally important enzyme, but also with other ones. In this connection, the toxicity of such a substance will also be determined by the competitive properties of the enzymes. For instance, the aliesterases contained in the fat-body and epithelium of an insect's intestine react actively with organophosphorus insecticides, decomposing them to non-toxic substances. Consequently, the toxicity of insecticides of this group grows when substances are added that inhibit the action of the aliesterases. The ability of a substance to surmount the enzyme barrier is taken into account in the synthesis of new pesticides.

Finally, the toxicity of a poison penetrating to the place of its action depends on the degree of affinity of a molecule of the poison to a molecule of the target. Although the target of most pesticides has not been established exactly, the necessity of such affinity of the molecules is confirmed by the fact that the toxicity of many substances depends on the structure of a molecule and the spatial arrangement of its atoms. As we have already noted, of all the isomers of hexachlorocyclohexane, the gamma-isomer is highly toxic to insects.

The mechanism of action of organophosphorus insecticides has been studied the most, therefore we can show the need of affinity of the poison molecules to those of the receptor using them as an example. All organophosphorus compounds must imitate the ester part of acetylcholine and contain a functional group capable of being adsorbed on the anion centre of cholinesterase. Otherwise, their toxicity to insects will be low.

2.5. Selective Toxicity of Pesticides

The **selective toxicity (selectivity)** is defined to be the ability of a substance to eradicate one species of living organisms without harming another one, even if the two species are in close contact with each other. The selective toxicity of pesticides with respect to various species of insects, animals, and plants is appraised according to the selectivity coefficient

$$K_{sel} = \frac{LD_{50} \text{ for one species}}{LD_{50} \text{ for the other species}}$$

Highly selective substances have a selectivity coefficient considerably higher than unity. Pesticides must have a low toxicity to beneficial plants, insects, mushrooms, animals, and humans. In a number of cases, this is very difficult to achieve owing to the similarity in the nature of the biochemical and physiological processes in the beneficial and harmful organisms or in connection with the fact that the harmful species dwells inside the plant being protected.

A substance having selective toxicity may act mainly in three ways: either the harmful species accumulates more of the substance, or it reacts with cellular structures present only in the harmful species, or it is capable of damaging a chemical system vitally important for the harmful species and having only a minor significance for the beneficial one.

Selectivity based on differences in accumulation signifies that the relevant substance is toxic to both beneficial and harmful organisms, but only the latter can accumulate it in a toxic dose.

In this case, the selectivity is determined by the features of application of the active ingredient, the behaviour and morphology of the organisms, and also by the processes of penetration of the poison, its metabolism and excretion from the organism. Such toxicity can be partly regulated by producing special formulations (granules, microcapsules) for the directed use of the pesticides.

The low toxicity of fungicides such as captan and folpet to plants is explained by their considerably lower penetration (2000-3000 times) into plant cells than into germinating condia and spores of fungi. The comparatively low toxicity of some organophosphorus insecticides to humans (bromophos, tetrachlorvinphos, fenitrothion, malathion) is due to the fact that in the organism of mammals these compounds are rapidly decomposed into non-toxic substances, while in the organisms of insects this process goes on more slowly or begins with activation of a molecule. The selectivity of many herbicides (barban, triazine derivatives) is also determined by the differences in the processes of detoxication of the substances in various plants.

Harmful and beneficial organisms have a number of cytological distinctions that are used as the basis of selectivity. Particularly, poisons acting on the nervous system (for example, HCH) are only slightly toxic to plants, but are toxic to animals. Substances decomposing the chloroplasts of plants are virtually unpoisonous to animals. Antibiotics inhibiting the synthesis of the cellular shells of bacteria have no toxic action on the cells of animals and humans, which do not have such shells.

Finally, many pesticides are selectively toxic because they act on biochemical processes specific or vitally important only to definite organisms. For instance, herbicides such as triazine and carbamate derivatives and thiocarbamates are only slightly toxic to humans and warm-blooded animals because they selectively inhibit the

process of photosynthesis inherent only in plants. Organophosphorus insecticides and acaricides do not suppress the growth and development of plants because they act on the processes of synaptic transmission of nerve pulses that are not inherent in plants.

2.6. Resistance of Harmful Organisms to Pesticides

The resistance of an organism to a pesticide is a biological property of the organism to withstand the poisoning action of the pesticide. A resistant organism functions, develops, and reproduces normally in a medium containing a poison. The phenomenon of resistance and the reverse phenomenon of sensitivity are closely related to the toxicity of the relevant poison, especially to its selective toxicity because all the factors causing toxicity also act on the resistance or sensitivity of an organism.

There are distinguished natural resistance based on the biological and biochemical features of an organism, and acquired, or specific, resistance appearing only because of interaction with the poison.

Natural resistance is subdivided into specific, sexual, phase (stage), age, seasonal, and temporary. This kind of resistance appeared and exists independently of the use of chemical means for plant protection.

Specific resistance is due to the features of the biology of definite species of harmful organisms (insects, mites, rodents, etc.). To overcome it, special pesticides are synthesized and used that have a selective toxicity (insecticides against insects, fungicides against the causal organisms of fungal diseases). The chemicals for plant protection include pesticides both with a narrow selectivity acting only on one species of harmful organisms or on several species of the same genus (pirimicarb against aphids, barban against wild oats) and with a broad spectrum of action (phosalone against insects and mites, DNOC against wintering forms of insects, fungi, and bacteria, and also against weeds). Hence, specific resistance can be successfully controlled by selecting the appropriate pesticide.

The resistance of organisms fluctuates greatly within a single species, which must be taken into account when using pesticides. In a number of cases, female specimens of insects and animals have a higher resistance to poisonous substances. Such a sexual resistance is overcome by choosing the relevant doses. Changes in the resistance of harmful organisms are also noted in ontogeny depending on the phase (stage) of development. The most sensitive to poisons are larvae and adult insects, fungal conidia at the time of growth, and plants in the germinating stage. A high resistance is a feature of insects in the egg and chrysalis stages and during the diapause, of wintering spores of fungi and bacteria, and of the seeds of plants.

The resistance of harmful organisms to poisons within a single stage (phase) of development changes depending on the age, time of the day and the year (season). The larvae of insects are more sensitive to insecticides at an early age, while toward the time of moulting their resistance increases. The resistance of plants and rodents also grows with their age. Insects wintering in the phase of imago or larva are characterized by seasonal resistance. At the end of summer or autumn, these species are more resistant to pesticides because they accumulate a considerable amount of fat and do not eat much. In the spring, they are more sensitive to poisons because their organism is weakened by the prolonged wintering. The main way of controlling seasonal, temporary, and age resistance is the proper choice of the pesticides and strict observance of the optimal periods for treating agricultural objects.

Specific (acquired) resistance signifies the ability of a harmful organism to survive and reproduce in the presence of a chemical substance that previously suppressed its development. The first reports on the appearance of races of pests that resist the action of chemical formulations relate to 1915-1916, when a race of red wild orange scale resisting hydrocyanic acid was discovered in California (USA). Later the appearance in other insects of a specific resistance to inorganic compounds—lead arsenate and sulphur—and to pesticides of a vegetative origin—pyrethrum—was noted. Up to the forties of the current century, no importance was attached to this phenomenon because pests became accustomed to poisons quite slowly, and they were controlled successfully. With the appearance of new synthetic pesticides, the acquired resistance of insects began to develop rapidly, and at present this is noted in over 200 species of insects. Specific resistance appears in the fifth to tenth generation of the harmful organism and develops to such an extent that in some regions it becomes impossible to use certain pesticides. In a number of regions, the resistance of the spider mite to metasystox increased from 100 to 500 times, and in the southern regions of the USSR the hawthorn mite on apple trees became from 30 to 40 times more resistant to organophosphorus acaricides. It has been found that upon the perennial application of the same fungicide, for instance benomyl, the resistance of fungi spores may increase from 3 to 12 times.

It has been established at present that the phenomenon of specific resistance is based on the selection from genetically heterogeneous populations of specimens having an increased resistance. The selecting factor is the pesticide. The effectiveness of this selection depends on the initial material (insects, mites, etc.), the number of treatments, the pesticide dose, and the genetic heterogeneity. Specific resistance appears more rapidly when a harmful organism produces more generations during a season, its heterogeneity is higher, and

the dose of the pesticide is smaller. The selected race of the pest, however, in the majority of cases is less adapted to the conditions of existence, and after discontinuation of the chemical treatments, the population in a certain time returns to its initial state. But when treatments with the same substance are renewed, the specific resistance appears more rapidly.

Specific resistance may be individual, group, and cross.

Individual resistance (only to one pesticide) is encountered quite rarely and is due to the activity of narrowly specialized enzymes decomposing the toxic substance. For example, the resistance of insects to malathion is explained by the fact that this pesticide is rapidly decomposed in the organisms of resistant insects by the enzyme malathionoxidase.

Group resistance is resistance to two or more pesticides that are related in their structure and mechanism of action and that belong to one group, appearing after the use of a substance of this group. For example, after treating insects with formulations of HCH, a race of pests appears that resists all organochlorine insecticides. The group resistance of insects or mites is due to the following reasons.

1. Slower penetration of a poison into an organism and faster excretion of it. Resistant specimens excrete from two to three times more toxicant than sensitive ones.

2. Rapid detoxication of a poisonous substance because of a higher activity of the enzymes or the appearance of specific enzymes. In races of insects resisting organophosphorus compounds, the activity of aliesterases and phosphatases is higher than in sensitive ones. As a result, an insecticide rapidly decomposes. Some species of insects have a set of specific enzymes that actively decompose insecticides (for instance, malathionoxidase in insects resisting malathion).

3. A different penetrability of the shells of nerve cords. In the organism of resistant insects, the insecticide penetrates poorly into the nerve cells (established for polychlorocyclodienes).

4. An increased lipid content in the body of resistant specimens. The result is the fact that lipid-soluble poisons are retained in the fat layer in a considerable amount and are removed from the sphere of action.

Cross resistance is resistance to two or more pesticides of different groups as regards both chemical structure and the mechanism of action that appears after the use of one pesticide. Such resistance is encountered rarely and has been studied very little. This phenomenon is apparently explained by the fact that a previously used insecticide increases the activity of the non-specific enzymes of the endoplasmic reticulum of the fat-body. Consequently, the new insecticide is rapidly decomposed to non-toxic products.

To manage resistant races of harmful organisms and prevent the appearance of specific resistance to pesticides, it is essential to strictly observe the rates of use of the formulations and the periods of their application. The basic factor in controlling acquired resistance is the alternation of pesticides with a different mechanism of action both during a season and from year to year. For example, phosalone is recommended for the first treatments of orchards against apple worms, and carbaryl for the following ones. In controlling mites, the use of dinobuton is alternated with dicofol treatment.

Specific resistance can be overcome by adding synergists to pesticides, i.e. substances that amplify their action. The integrated method of protecting plants is effective in combatting specific resistance. This makes it possible to prevent the appearance of resistance of harmful organisms to pesticides, diminishes the danger of affecting entomophags and lowers the contamination of the environment with the toxic residues of pesticides.

Chapter 3

INFLUENCE OF PESTICIDES ON ENVIRONMENT

The continuing intensive chemization of the world's agriculture leads to a large amount of various chemicals, including pesticides, being introduced every year into the planet's biosphere—the habitat of all living beings including man. This is why the problem of protecting the environment from chemical contaminants has acquired a major significance.

Pesticides, as possible contaminants of the environment, are characterized in comparison with other chemicals by the following features:

(1) the impossibility of preventing their circulation in the biosphere (when sprayed with the aid of aerial and surface equipment a pesticide immediately gets onto objects of the environment and remains there until it decomposes completely);

(2) the biological activity of the pesticides owing to their purpose, which creates a potential danger to nature and man;

(3) the impossibility of decreasing the rates of use owing to the necessity of ensuring a high effectiveness of the protective measures;

(4) contact of pesticides with large bodies of the population, which is associated with the use of pesticides in various branches of the economy, their circulation in the environment, and the presence of residues in food products;

(5) the persistence of pesticides in natural conditions and their transfer along the food chains;

(6) the possibility of the accumulation of pesticides in organisms coming into contact even with low concentrations thereof, up to a biologically active level.

Depending on the features of pesticides, the following forms of their action in the biosphere are distinguished.

1. Local action: (a) directly on harmful organisms; (b) secondary on other organisms, the soil, water.

The effectiveness of local action of pesticides is determined by the dose, form, way of application, selectivity, and rate of decomposition.

2. Nearest aftereffect (landscape-regional). With respect to the duration and nature of action, it varies depending on the relief, soil, and climatic conditions. A dry climate, large salinity of the soil, and close (high) ground water table are factors increasing the probability of the persistence and repeated accumulation of stable pesticides and their metabolites in the soil, water, and biomass.

3. Remote aftereffect (regional-basin). It is characteristic of very stable pesticides capable of migrating into river basins, along their flood-plains and terraces. The pesticides may migrate in the form of solutions, suspensions, or in the sorbed state with soil colloids. Migration, redistribution, and accumulation in flood plains, deltas, and estuaries may continue from 3 to 5 years and more. As a result, the pesticides may act on organisms in the lower reaches of rivers, deltas, and in the sea.

4. Very remote (global) aftereffect. It covers the planet as a whole and its individual components—the ocean, land, and atmosphere. It is associated with the transfer of persistent poisonous chemicals in the form of solutions, aerosols, and suspensions by air currents; by coastal and transocean currents, storms, cyclones; by the migration of birds, animals, and humans; by the movement of means of transportation and freight, raw materials, and food products; by the testing of nuclear and other weapons, and by military operations.

Such aftereffects manifest themselves gradually. They are weakened by factors such as insolation, ultraviolet radiation, electrical discharges, atmospheric precipitation, and burying in the marine deposits of seas and oceans. The possible general aftereffects on living organisms may probably tell only in a few generations provided that considerable amounts of poisonous chemicals accumulate on various continents and in the oceans (V. Kovda, 1976).

Hence, pesticides, which are an important factor in mankind's action on the environment, may also exercise various by-effects on it (Table 2).

These by-effects, depending on the degree of their manifestation, can be divided into three categories.

1. The development of resistance of harmful organisms to pesticides. It is associated with the stability and accumulation of residues

Table 2. By-Effects of Pesticides on the Environment (after N. Van-Teal, 1975)

Elements of environment	Potential by-effects
Abiotic environment	Presence of residual amounts in soil, water, and air
Plants	Presence of residual amounts
	Damage because of phytotoxicity
	Changes in the vegetative development (when herbicides are used)
Animals	Presence of residual amounts in domestic and wild animals
	Physiological actions (non-vitality of birds' eggs)
	Extermination of definite wild species (mammals, birds, fish)
	Extermination of beneficial, harmful, and entomophagous insects
	Change in the number of insects (development of second-generation pests as a result of eradication of beneficial, harmful, entomophagous insects)
Man	Presence of residual amounts in tissues and organs
	Occupational diseases
Food	Presence of residual amounts
Organisms being controlled	Development of resistance

of pesticides and is due to the succession of populations as a result of a transition from sensitive specimens to resistant ones of the same species owing to selection caused by the action of the pesticide. The physiological and biochemical nature of the resistance, the reasons for its appearance, and the ways of overcoming it were treated above.

2. The influence of pesticides and their residues on plants, animals, and their environment (damage and a change in plants, changes in the composition of the microflora, the perishing of mammals, birds, fish, or beneficial insects). This influence may lead to the development of secondary pests owing to the vanishing of definite species of predators and parasites that in normal conditions could keep a potential pest at a level below its economical harmfulness.

In other words, pesticides may affect biocoenoses.

3. Accumulation and transmission along food chains. The residues of pesticides in the environment may be absorbed by plant or animal organisms, which, in turn, are eaten by larger species of animals in which the concentrations of the poisonous chemicals being accumulated grow. This leads to the presence of residues of pesticides in food and their subsequent consumption by humans.

The circulation of pesticides may occur according to the following schemes:

air—plants—soil—plants—herbivorous animals—man;
soil—water—zoo- and phytoplankton—fish—man

For example, 1 kg of soil may contain only thousandths of a milligram of organochlorine pesticides, whereas carrots grown in this soil may contain from 1 to 6 mg of pesticides per kilogram of the vegetable. Some pesticides enter plants through their root system, and as the fruits grow the concentration of the pesticides in them increases. Some plants and all animals are capable of accumulating and retaining organochlorine poisonous chemicals in their organism for a long time.

What has been said above shows that the path along which the residues of pesticides reach human beings is through their food. For this reason, a safe barrier must be erected between man and his food, i.e. tolerance levels of pesticides.

The **tolerance levels** of pesticides in food products are the officially allowed harmless amount of them in food in milligrams per kilogram of the relevant product. All the procedures followed in storing, processing, and preparing food products facilitate the diminishing of the pesticide residues in the food.

To understand correctly how pesticides affect the environment, we must consider the behaviour of pesticides in separate ecosystems and their influence on the most important objects of these systems.

3.1. Behaviour of Pesticides in the Air

The treatment of agricultural crops, seeds, forests, and water basins with pesticides is the main source of their supply into the air. It is exactly transportation by air that can explain the broad occurrence in the environment of persistent pesticides, which can be detected at a considerable distance from the places of their use.

In finely dispersed spraying, especially upon aerial treatment, the pesticides may be adsorbed by the solid particles in the air and be transported by the air currents. It has been established, for example, that when a pesticide is sprayed over a forest, only about 50% of it remains on the trees of the relevant area. The remaining amount stays in the air for a certain time, and then settles onto plants and the soil at a considerable distance from the place of treatment. The deflection is especially large when highly volatile insecticides are used. The air is polluted more when dusts are used than when sprays are.

Pesticides get into the air together with soil dust in wind erosion, and also when cultivating the soil and when harvesting the crop.

A considerable amount of pesticides is detected in the atmospheric dust in regions where intensive chemical treatments are practised.

Pesticides may get into the air from moist surfaces as a result of evaporation together with water vapour and of evaporation from the surface of the soil and plants.

Hexachlorobutadiene used for controlling the root form of phylloxera in vineyards has been found to enter the atmosphere from the fumigated soil.

The degree of pollution of the atmospheric air with pesticides depends on their physicochemical properties, the temperature of the air, the speed of the wind, the area being treated, and also on how the substance is applied. The highest concentrations of pesticides in the air are registered in the midday when the temperature of the air reaches its maximum value.

Pesticides are removed from the atmosphere together with precipitation, in the course of diffusion in the boundary layer of the air and the ocean, and also as a result of chemical decomposition. From the atmosphere, the pesticides and their metabolites get into water, the soil, and continue to circulate in the environment.

3.2. Behaviour of Pesticides in Water

Water is the main means of transporting pesticides in the environment. Poisonous chemicals may get into open basins with the sewage of enterprises producing pesticides, in the aerial and surface treatment of agricultural lands and forests, with rain water and melted snow, and also upon the direct treatment of open basins to destroy algae, mollusks, vectors of disease-spreading organisms infecting man and animals, and weeds.

Soil and ground water, inland basins, rivers, and the oceans in definite conditions may become the terminal station for pesticides. Consequently, the pollution of basins first of all with persistent pesticides is possible. Residues of organochlorine compounds such as dichlorodiphenyltrichloroethane (DDT), HCH, and toxaphene have been detected in the water of open basins in different countries, but only in rare cases were concentrations reaching a dangerous level noted. Special studies conducted in the USA in 1966-1968 showed that in 41% of the analysed river water samples, the concentration of pesticides was at the level of 0.001 mg/litre, and in 8% of the samples reached 0.012 mg/litre (V. Vasilyev, 1975).

The accumulation of persistent organochlorine insecticides in the ooze of water basins is of great significance. This may lead to secondary pollution of the water when it is roiled.

Some insecticides in insignificant concentrations may change the organoleptic properties of water (its odour, taste), have a negative effect on the processes of oxygen formation by phytoplankton, on the

vital activities of the inhabitants of the water ecosystems, be transmitted along the food chains, and accumulate in food products.

The influence of pesticides on the inhabitants of water systems may manifest itself both in direct toxic action (acute or chronic toxicity) and indirectly (diminishing of the content of oxygen dissolved in the water, a change in the chemical composition of the water, extermination of water insects, etc.).

When pesticides pass over from water into other links of the biological chain, their content grows hundreds and thousands of times. Being absorbed by a filtering organism (for example, by one of the species of plankton organisms), persistent poisonous chemicals may be deposited in the tissues and then get into the organism of a fish. In the following links of the food chain, the action of the pesticides, being cumulative, is amplified several times. For instance, when organochlorine pesticides are washed by rain water sewage into water basins in an amount of 0.00003 mg/litre, they are found in fish in an amount of 1-7.4 mg/kg, and in crawfish in an amount of 0.5-0.7 mg/kg (Hopkins, 1966).

The ability of toxaphene to accumulate in water-food chains is especially great. For instance, when its concentration in a lake was 0.0002-0.0006 mg/litre, there was found: in water plants 0.2-0.4, in water invertebrates 0.5-1.4, in trout 3.5-5.7, and in salmon 1.8-3.4 mg/kg (Terrier, 1966). The degradation of toxaphene occurs very slowly: for example, during six years its content in the water diminished insignificantly.

It must be noted that the toxicity of pesticides to various species of fish and other water inhabitants varies and may change within very broad limits. As a whole, organochlorine pesticides are the most dangerous, while organophosphorus ones and derivatives of carbamic acid are the least dangerous. In certain classes of compounds, however, the fluctuations in the toxicity to fish are very noticeable, which is associated with the different mechanism of their action on fish not only for individual classes of compounds, but also for individual pesticides.

Special mention must be made of the behaviour in water of herbicides introduced into closed water basins to suppress the development of either higher water plants (submerged, semisubmerged, with floating leaves) or lower algae (phytoplankton and phytobenthos). It has been established that as the active ingredient dissolves in the water and diffuses over the basin, the herbicides affect all other components of the aqueous ecosystem: the microorganisms, bacterio-, phyto-, and zooplankton, phyto- and zoobenthos, neuston, fish, and amphibians. This influence also extends to the hydrochemical conditions of the basin (the content of oxygen, carbon dioxide, the pH, carbonate equilibrium, the dynamics of various forms of nitrogen, organic components) (L. Braginsky, 1975). The reactions

of the microflora of water basins to herbicides exhibits most clearly the growth in the number of saprophytic microorganisms (in 2-3 weeks after treatment). Some herbicides (diuron, monuron) have a sterilizing action. Changes are observed in the number and functional activity of ammonifiers, nitrifiers, and denitrifiers, which results in the accumulation of ammonia and nitrates in the basin.

Herbicides have the largest action on aqueous animals. While not having a pronounced acute toxicity and not leading to phenomena of visible poisoning, herbicides nevertheless cumulate in the organs and tissues of hydrobionts. The most sensitive components of zooplankton are the *Cladocera* suborder, which perish in the third to fifth generation. Animals also perish because of the shortage of oxygen, which is the result of its increased consumption upon the extermination of plants or the decomposition of phytoplankton, and also because of the suppressing of the photosynthesis activity of plants and of their stopping to produce oxygen. The resultant prolonged and sharp deficit of oxygen leads to the death of fish, amphibians, and invertebrates. Violations of metamorphosis are also noted in air and water insects (midges). The embryonic and larval stages of development of fish and invertebrates were found to be especially sensitive to the action of herbicides.

The cycle of nitrogen, carbon, and oxygen in a water basin is violated. As a whole, however, the ecosystem of basins treated one time with herbicides becomes restored quite rapidly (in a few weeks or months) depending on the dose of the herbicide, its formulation, the specific composition of the plants, the biomass that was decomposed, the rate of flow of the water, the physicochemical features of the soil, and other conditions (L. Braginsky, 1975; T. Khripko, 1976). A comparative appraisal of various formulations of herbicides (wettable powders, suspensions, emulsions, granules) showed the considerable differences in their action on aqueous ecosystems. Treatment of the bottom of unwatered or drained ponds with granulated herbicides or the local introduction of granules in spring at the earliest stages of development of weeds (at 15-16 °C) is safer for the environment.

As a rule, many pesticides rapidly decompose in an aqueous medium, and in this connection their use in agriculture for managing pests, diseases, and weeds of agricultural crops does not lead to negative consequences.

3.3. Behaviour of Pesticides in the Soil

Pesticides are introduced into the soil for destroying soil-dwelling pests, nematodes, and the pathogens of bacterial and fungal diseases. Herbicides are widely introduced into the soil. Pesticides also get into the soil after treatment of the green organs of plants: they

are washed off by atmospheric precipitation and carried off by the wind.

Pesticides may get into the soil in the form of their residues contained in leaves, roots, etc. Depending on the conditions, poisonous chemicals may remain in the soil unchanged and retain their toxicity for a more or less prolonged period.

The property of pesticides to withstand the decomposing action of physical, chemical, and biological (biochemical and microbiological) processes characterizes their **persistence.**

The persistence of various compounds when studied in the same conditions (or of the same compound, but in different soils), is characterized by the parameter $T_{0.5}$ (the half-life). The latter denotes the time during which the content of the relevant pesticide in the soil is halved in comparison with the original amount. To evaluate this parameter, soil samples are taken and analysed from a dynamic viewpoint in logarithmically multiple intervals. By determining in the same intervals the dynamics of the content of pesticide residues in cultivated plants, one can evaluate the parameter $T_{0.5}$ and the harvest time. It must be noted that a pesticide getting into the soil may decompose into a whole series of metabolites whose persistence, phytotoxicity, features of behaviour and transformation in the soil must be studied just as thoroughly as those of the original substances.

The persistence of pesticides in the soil depends on their chemical and physical properties, the dose, formulation (powder, liquid, etc.), the type of soil, its moisture content, temperature, and physical properties, the composition of the soil microflora, the specific composition of the growing plants, and the features of soil tilling.

With respect to the rate of their decomposition in the soil, pesticides can be divided into the following groups.

1. Organochlorine insecticides—a decomposition period over 18 months.
2. Derivatives of triazine, urea, and picloram—about 18 months.
3. Derivatives of benzoic acid and amides of various acids—about 12 months.
4. Phenoxyalkylcarboxylic acids, nitriles, derivatives of toluidine—6 months.
5. Derivatives of carbamic acid—up to 3 months.
6. Organophosphorus substances—less than 3 months.

It must be noted that in many cases the type of soil and especially its microflora are the main factors determining the duration of decomposition of most pesticides. Even very persistent substances under the influence of certain microorganisms may rapidly decompose with complete destruction of the molecules.

Pesticides incorporated into the soil in the form of granules persist in it for a longer time than powders or liquid substances. Pesticides,

as a rule, are more persistent in soils with a high content of organic matter and a silt fraction.

Movement of Pesticides in the Soil. Pesticides and their metabolites are found in the soil in a labile state with all three of its phases and can therefore migrate along the soil profile in a horizontal and vertical directions.

Poisonous chemicals move in the soil owing to molecular diffusion with the capillary moisture, the descending flow of gravitational water, the root system of plants, and as a result of displacements when the soil is being tilled. Pesticides travel over larger distances with the stream of water appearing after rainfall or irrigation. The rate and depth of vertical movement depend on the solubility and dose of the pesticide, the features of its adsorption and desorption, its volatility (vapour pressure), and also on the intensity of evaporation of the soil moisture. During prolonged rainfall or irrigation, poorly adsorbed hydrophilic pesticides move downward along the soil profile together with the water. With the advent of dry weather, with increased evaporation, the pesticide solution rises along the capillaries to the surface of the soil. When evaporation and washing out are in equilibrium, pesticides well soluble in water travel downward, while poorly soluble ones are retained in the upper layer of the soil. If the concentration of a poisonous chemical in the soil solution diminishes owing to decomposition, washing out, or evaporation, part of the pesticide adsorbed by the colloids in the soil may again enter the soil solution owing to desorption.

Investigations have shown that HCH migrates insignificantly in the soil. The pesticide is mainly distributed in the soil as a result of its mechanical cultivation. Carbaryl in chernozem, gray forest, and soddy-podzolic soil penetrated to a depth of 50-70 cm, which is associated with its very slight adsorption by the soil colloids. In sandy loam soil, HCH migrates better than heptachlor. Among herbicides, derivatives of the aromatic carboxylic acids have the highest mobility in soil, and toluidine derivatives, the lowest mobility. Dipyridyl herbicides, which are greatly adsorbed by the soil, do not virtually migrate along its profile. Even in sand, diquat moves not deeper than 8 cm.

The derivatives of phenylacetic and benzoic acids, weakly adsorbed by the soil and well soluble in water, can migrate to a depth of up to 3 m.

Herbicides that are derivatives of 2,4-D and MCPA are poorly washed out of the soil because they are bound by the soil colloids. Esters of 2,4-D are washed out from the soil much more easily than salts. The derivatives of urea also migrate poorly in the soil. Triazine herbicides (simazine, atrazine, prometryne, propazine) owing to their slight solubility in water and great adsorption by the soil migrate in the latter to a limited extent.

Decomposition of Pesticides in the Soil. Pesticides become modified or completely decomposed in the soil as a result of physicochemical processes, microbiological decomposition, and the absorption by higher plants and the soil fauna. Many pesticides become detoxicated owing to their adsorption by humus and other colloids or to the formation of stable complexes in the soil. Poisonous chemicals

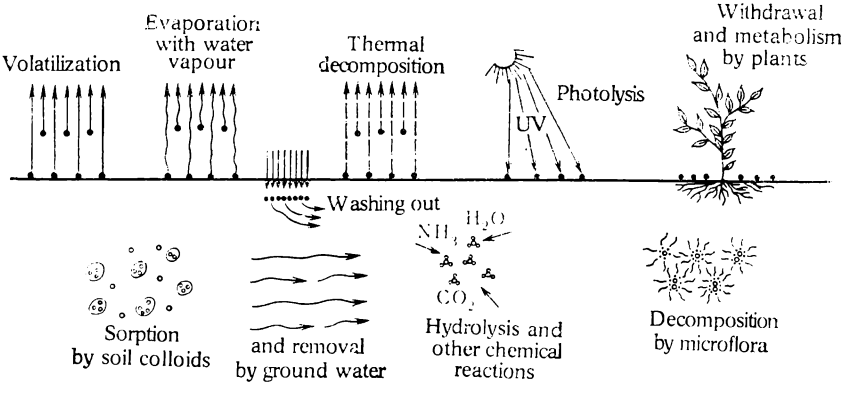


Fig. 2. Detoxication of pesticides in soil

are removed from the soil as a result of volatilization, evaporation with water vapour, migration beyond the root-habitat layer, washing out by rain water, melted snow, irrigation, ground, and soil water (Fig. 2).

The basic criterion of the detoxication of pesticides in the soil are the rate and completeness of their decomposition into non-toxic components.

The determining role of individual processes in the inactivation of pesticides in the soil depends not only on the physicochemical properties of the pesticide and its formulation, but also on the properties of the soil, the climatic and ecological factors.

Role of Physical Factors in Pesticide Inactivation in the Soil. Pesticides incorporated into the soil lose a part of their activity because of their being adsorbed by the soil colloids. The degree of adsorption of most pesticides largely depends on the humus content in the soil. Most insecticides and soil herbicides are adsorbed to a larger extent by humous soil than by loam and sandy loam. In the adsorption of pesticides, the adsorption surface of the soil and the degree of its affinity to a given pesticide (the magnitude of the surface energy) are of major importance. For example, triazine derivatives are easily adsorbed by negatively charged soil colloids owing to cation exchange. The affinity of the molecules of these

herbicides to the organic matter of the soil is higher than to inorganic clay minerals. The origin of the organic matter is of importance here. In the humin, humic acid, and fulvic acid fractions of humus, the capacity of adsorbing pesticides diminishes in the order in which they are listed.

The dependence of the adsorption of some pesticides on the pH, pK, and hydrolytic acidity of the soil has been established. For instance, linuron, diphenamid, and picloram are adsorbed at a higher rate with an increase in the pH of the soil. Conversely, the adsorption of 2,4-D and MCPA grows when the pH of the soil solution decreases. Simazine is adsorbed more in soils with an increased hydrolytic acidity. In addition to the content and properties of the soil humus, of great significance for the adsorption of pesticides are the mechanical composition, the content of the clay and silt fractions.

The degree of adsorption of pesticides depends not so much on the content of the clay and silt particles in the soil as on the nature and origin of the clay minerals that are distinguished by the magnitude of the surface of the particles and the structure of their crystal lattice. Consequently, the nature of adsorption of a pesticide will vary depending on whether an anion or a cation is the active part of a pesticide molecule, or whether its molecule is ampholytic or electrically neutral and does not dissociate. For example, montmorillonite adsorbs many pesticides very well, which is the result of its property of binding ions and molecules not only on the surface of the mineral, but also in the intermolecular spaces.

The degree of adsorption of pesticides by the soil depends greatly on its moisture content. The larger the amount of water absorbed by the colloids, the smaller is the amount of free space remaining for the sorption of poisonous chemicals.

The nature of adsorption depends on the chemical structure of the pesticide, its basicity, and on the properties of its functional groups to form hydrogen and dipole bonds. In herbicides that are triazine derivatives, the degree of adsorption by the soil increases in the following order: propazine, atrazine, simazine, prometryne; in urea derivatives—dichloralurea, fenuron, monuron, diuron, linuron.

When the adsorption of pesticides by clay minerals was studied, it was established that hydrogen bonds exist between the carboxyl, methyl, and methylene groups of the compounds and the surface of the minerals.

The adsorption of poisonous chemicals in the soil also depends on its temperature. This is of a practical significance because triazine herbicides incorporated into the soil in cold and damp weather are adsorbed in the top layer of the soil, which prevents their being washed out or decomposed. Becoming desorbed when the weather gets warmer, they again exhibit their activity.

Precipitation and elevation of the temperature facilitate the desorption of pesticides absorbed by the soil.

Evaporation with water vapor is one of the factors leading to the loss of toxicity in the soil of insecticides such as heptachlor. It has been established that non-polar pesticides evaporate to a greater extent than polar ones.

The losses of toxic chemicals in the soil because of volatility are mainly characteristic of pesticides with a high vapour pressure such as EPTC, pebulate, and trifluralin. The volatilization of these pesticides depends on the moisture content of the soil. For example, in 15 minutes after treatment with EPTC, the losses of its vapour from dry soil amounted to 20%, from moist soil, to 27%, and from wet soil, to 44%. The vapour of a volatile pesticide is adsorbed by dry soil to a considerably greater extent than by moist soil. This allows us to treat dry soil with volatile pesticides without any risk of lowering their effectiveness.

The incorporation of such substances immediately after treatment to a depth of 5-7 cm appreciably diminishes their losses in the vaporous form and is an obligatory procedure when volatile soil herbicides are being used.

Pesticides may also decompose in the soil under the influence of elevated temperatures. For instance, the activity of atrazine, simazine, diuron, monuron, and fenuron in soil experiencing the action of high temperatures (40-82 °C) diminishes by 40-97%. Such heating of the soil's surface layer is quite possible in field conditions on a very hot sunny day.

Physicochemical and Chemical Decomposition of Pesticides in the Soil. Pesticides may decompose under the action of solar radiation. A marked role is played by the ultraviolet rays of this radiation in the process of photooxidation of certain pesticides and their metabolites. Many herbicides, especially dipyridyl preparations such as diquat, lose their toxicity under the action of solar radiation. The resulting metabolites have a low toxicity to warm-blooded animals.

The hydrolytic and oxidation transformations of many pesticides in the soil appreciably lower their toxic action. An important role is played by the chemical structure of the pesticide and its properties. The kind and number of halogen atoms and their arrangement in a molecule affect the rate of decomposition of pesticides that are derivatives of halogenated and aromatic carboxylic acids. The length of the hydrocarbon chain in aliphatic acids also affects the persistence of such pesticides. Metasubstituted chlorophenylcarbamates decompose more rapidly than ortho- and parasubstituted ones. The number and position of the chlorine atoms in the benzene ring affect the rate of decomposition not only of the ring, but also of the side chain. Among triazine herbicides, the fastest to decompose are me-

thylthio derivatives, the slowest are methoxy derivatives. Chlorine-substituted triazines are intermediate in their persistence.

Decomposition of Pesticides by Soil Microorganisms. The decomposition of most pesticides in the soil is associated with microbiological activity. Better conditions for the development of the soil microorganisms are attended by more intensive microbiological decomposition of the poisonous chemicals.

The mechanism of metabolism of pesticides in the soil under the influence of microorganisms consists in the following main reactions: dehalogenation, dealkylation, amide or ether hydrolysis, oxidation, reduction, breaking of an ether bond, hydroxylation of an aromatic ring, and breaking thereof.

The nature of decomposition of organic compounds depends on the features of the enzyme produced by the microorganisms. In a number of cases, several enzymes produced by various microorganisms are responsible for this decomposition at definite stages. As a rule, aromatic substances with a cyclic structure decompose considerably more difficultly than compounds of the fatty series. The decomposition of cyclic compounds begins with oxidation of the side groupings and their detachment. Next the carbons of the ring are oxidized and breaking of the aromatic compound occurs; if it contains two or more rings, they decompose consecutively.

Dehalogenation consists in the detachment of a halogen atom from a pesticide molecule. For herbicides that are derivatives of aliphatic acids (TCA, dalapon), this process is the common initial reaction of inactivation. Derivatives of the aromatic series are dehalogenated with the formation of one or more decomposition products.

Of major significance for the dehalogenation of pesticides is the number, position, and kind of halogen atoms in the compound. An increase in the number of halogen atoms in a pesticide molecule, and also an increase in the distance from the functional group lowers the rate of the decomposition reaction. This is why a compound with a halogen in the paraposition is decomposed more readily than when it is in the metaposition.

The enzymatic dechlorination of simple aliphatic acids occurs when a chlorine atom is replaced by a hydroxy group. Breaking of the bond —C—Cl in dalapon leads to the formation of pyroracemic acid derivatives.

The dealkylation of pesticides in the soil may take place with breaking of the bond C—R, N—R, or O—R. Dealkylation is a nonhydrolytic way of decomposing some groups of herbicides in the soil. These groups include secondary amines of dialkyl-1,3,5-triazines (simazine), tertiary amines of dimethyl derivatives of phenyl urea (diuron), dinitrotoluidines (trifluralin), quaternary ammonium salts of pyridine, herbicides with an ether or ester bond (2,4-D, MCPA).

The hydrolytic way of decomposing pesticides in the soil is characteristic of compounds including in their composition amides and ethers. The main ones of them are phenyl carbamates (chlorpropham) and acetamides (propanil). Their hydrolysis in the soil consists in breaking of the amide or ether bond and the formation of aniline, carbon dioxide, and an alcohol (in phenyl carbamates), or aniline and an aliphatic acid (in propanil). Hydrolytic decomposition is associated with the rapid detoxication of the initial substance.

The oxidation of pesticides in the soil by microorganisms proceeds very diversely. For example, relatively stable organochlorine compounds having a double bond may be oxidized to epoxides. Prometryne is metabolized by soil microorganisms to a sulphoxide, and then to a sulphon. The fatty acids formed in the primary oxidation of aliphatic hydrocarbons are decomposed with the aid of the β-oxidation mechanism to acetic acid via a number of intermediates.

Oxidation plays an important role in the decomposition of herbicides—derivatives of phenoxyalkylcarboxylic acids.

Organochlorine insecticides, as a rule, are the most resistant to microbiological decomposition in comparison with other derivatives (phosphorus-containing compounds, carbamates), but microorganisms oxidize heptachlor to heptachlor epoxide. The gamma-isomer of HCH (lindane) in the soil is metabolized under the action of *Clostridium sp.* via reduction dechlorination and hydrolysis with the formation of gamma-pentachlorocyclohexane. Trichlorophenol is formed as an intermediate.

Organophosphorus insecticides are also decomposed in the soil with the participation of microorganisms. For example, parathion-methyl decomposes in heavy loamy soil the most intensively with an increased moisture content and at a temperature of 30 °C; this is associated with hydrolysis or reduction to the amino form.

Fungicides are the least liable to microbiological decomposition in the soil because of their strong bactericidal and fungitoxic action.

The rate of herbicide decomposition increases markedly when the moisture content and temperature of the soil grow.

The process of decomposition of 2,4-D and other pesticides is preceded by a lag period during which no decomposition of a substance by microorganisms occurs, and the soil, as it were, is enriched with definite forms of microflora.

The microorganisms decomposing 2,4-D include the bacteria *Mycoplana sp.*, *Corynebacterium sp.*, *Bacterium globiforme*, *Achromobacter sp.*, *Flavobacterium aguative*, the actinomyces *Nocardia sp.*, *N. opaca*, and *N. coeliaca*. The group of bacteria *Arthobacter sp.* can use 2,4-D as a source of carbon.

Chlorinated aliphatic acids may be dehalogenated in the soil by microorganisms of the genus *Arthobacter*. Sodium trichloroacetate may also be decomposed in the soil by the action of the bacteria

Pseudomonas sp., *P. dehalogens*, and of the fungus *Trichoderma viride*.

The bacteria *Pseudomonas sp.*, *P. dehalogens*, *Agrobacterium sp.*, *Micrococcus sp.*, *Alcaligens sp.*, *Baccillus sp.*, the soil fungi *Trichoderma viride*, *Aspergilles sp.*, *P. lilacinum*, and the actinomyces *Nocardia sp.* can use dalapon as a source of carbon.

Herbicides that are derivatives of triazine are also decomposed in the soil by microorganisms. Simazine may be a source of nitrogen nutrition for a number of microorganisms (species of the genera *Bacterium*, *Microbacterium*, *Achrobacterium sp.*, *Empelobacterium*, etc.).

Herbicides that are derivatives of carbamic and thiocarbamic acids, for example chlorpropham, are decomposed in the soil by the microorganisms *Pseudomonas striate*, *Agrobacterium*, *Achromobacter*, which use the herbicides as a carbon source.

Herbicides that are urea derivatives are decomposed in the soil by the bacteria *Pseudomonas sp.*, *Xanthomonas sp.*, *Sarcina sp.*, *Baccillus sp.*, and by the fungi *Peniccillium sp.* and *Aspergillus sp.* These microorganisms are capable of utilizing monuron as the only source of carbon.

E. Mishustin (1964) stressed the fact that there are no forms of organic natural and artificial compounds which were never used as sources of nutrition by definite species of soil microorganisms. It is only essential that these compounds be used in concentrations that are not toxic to the given organisms.

Absorption and Detoxication of Pesticides by Plants. The accumulation of persistent pesticides in the soil in a number of cases leads to their translocation into the stems, leaves, and root vegetables. The level of the content of a pesticide in a plant is determined by absorption, the supply, and decomposition of the toxicant in the plant and the soil. As a whole, the intensity of migration of a pesticide from the soil into a plant and its accumulation in the productive organs depend on its content in the soil, although there is not always a direct relation between these parameters. The absorption and removal of pesticides from the soil by plants depend to a considerable extent on their specific features. It has been established that when HCH is introduced into the soil, carrots can accumulate it in their roots in amounts considerably exceeding the content in the soil. Plants can be arranged in the following order with respect to the degree of accumulation of organochlorine pesticide residues in the productive organs: carrot > parsley > potato > beet > perennial grass > tomato > corn > cabbage, and cauliflower. Organochlorine pesticides are accumulated mainly in the skin, to a smaller extent in the tops, and in a minimum amount in the pulp of root vegetables (K. Stefansky, 1973).

The crop being cultivated affects the content of pesticides in the soil and the rate of their detoxication.

As a whole, the detoxication of pesticides proceeds more intensively in tilled crops and in a fallow field.

Most herbicides are rapidly metabolized in resistant plants. A special role in the removal of herbicides from the soil belongs to plants resisting them owing to their having rapid detoxication mechanisms.

Influence of Pesticides on Activity of Soil Microflora and Fauna. Pesticides incorporated into the soil may change the composition of the soil microflora. Organochlorine insecticides in the doses recommended for controlling soil-inhabiting pests do not have a negative influence on the number of soil microorganisms.

Rapidly decomposing organophosphorus insecticides in the recommended doses stimulate the development of separate groups of microorganisms, and in increased doses first cause suppression, and then stimulation of the soil microflora.

A varying sensitivity to the action of organophosphorus insecticides has been noted in soil microorganisms. When the cellular structure of the microorganisms is more complicated, an increased sensitivity to these compounds is observed. At the same time, these insecticides act as a variability factor of the microorganisms involving their morphological, cultural, and physiological characters.

Soil fungicides and fumigants, as a rule, have a negative effect on the soil microflora.

The biological activity of the soil or the intensity of soil respiration (the absorption of O_2 and the evolution of CO_2) may be used as a general parameter showing how pesticides act on the soil microflora.

The change in the activity of the soil enzymes in definite conditions characterizes the effect of pesticides on the microbiological activity in the soil. The effect of pesticides on biological processes in the soil comes to light the most clearly only upon a repeated or multifold application of the toxicants.

Herbicides decompose comparatively rapidly in the soil, and their use in the recommended doses as a whole does not affect the soil microflora negatively. When herbicides are incorporated into the soil, especially in increased doses, a temporary regrouping occurs in the composition of the microflora. The action of herbicides on separate groups of microorganisms manifests itself differently within the limits of each systematic group. After incorporation of the herbicides, a short period of depression of the microflora activity sets in. The latter is restored owing to the appearance of resistant mutant forms or to the formation of enzymes that hydrolize the herbicide.

The nature of herbicide action on the microflora of the soil depends in many respects on the features of the structure and properties of the substances. Herbicides that are derivatives of phenoxycarboxylic acids (2,4-D, MCPA, 2,4-DB, MCPB, MCPP) do not have an inhibit-

ing action on the soil microorganisms in their recommended doses. It has been established that phenoxybutyric acids (MCPB, 2,4-DB) are much more toxic to soil microorganisms than the phenoxyacetic analogues corresponding to them.

2,3,6-TBA during the first four weeks after its incorporation lowers the activity of some species of soil microorganisms, inhibiting the process of nitrification. Sodium trichloroacetate (TCA) immediately after introduction may inhibit the active soil microflora, while dalapon stimulates its activity. Picloram even in large doses does not suppress the development of the main species of soil bacteria and fungi, does not affect the evolution of CO_2 by the soil and the hydrolysis of urea. It must be stressed that it is just the indifference of the soil microflora to picloram that explains its prolonged toxic action.

Herbicides that are triazine derivatives do not affect the development of most soil microorganisms in their conventional doses. Simazine and atrazine stimulate somewhat the activity of *Azobacter* and *Clostridium pasterianum* without affecting *Nitrosomonas*, but to some extent inhibit the oxidation of nitrites to nitrates under the action of *Nitrobacter*. The development of ammonifying, denitrifying microorganisms and rhizosphere microflora is stimulated under the action of these substances. The inhibiting action of simazine manifested itself in the development of soil algae. The most sensitive were blue-green algae. Carbamates and thiocarbamates initially suppress the activity of microorganisms. Isopropyl-N-phenyl carbamate can inhibit the activity of nitrifying bacteria.

Urea derivatives in conventional doses do not inhibit the development of soil microorganisms, but do exhibit a rather strong algicidal action.

The nature and degree of action of pesticides on soil fauna are due to the properties of the substances, their content in the soil, the composition of the fauna, and to the soil and climatic conditions.

In some cases, pesticides stimulate the reproduction of the soil fauna, in others they cause its suppression and extermination.

Unstable, rapidly decomposing pesticides are less dangerous to the soil fauna. Persistent compounds upon their surplus accumulation are a great danger.

Organochlorine insecticides such as HCH, heptachlor, and toxaphene in their usually recommended doses act weakly on or are completely harmless to earthworms, nematodes, and *Oligochaeta* (*Ehchytracidae*), but are toxic to the soil arthropods (springtails, mites). Organophosphorus insecticides have a short action on the soil fauna.

Most fungicides and herbicides also have an insignificant influence on the soil fauna because they decompose comparatively rapidly in the soil.

3.4. Action of Pesticides on Biocoenoses

The initial groups in every biocoenosis are plant-killing insects (phytophags). Their number is controlled by entomophags—their predators and parasites.

In an agrobiocoenosis with monotonous sowing or planting as regards the specific composition, a sharp reorganization of the collection of phytophags occurs: the species that cannot feed on the cultural plants and stand the conditions of their cultivation are sharply suppressed, whereas the species feeding on these plants find favourable conditions and become dangerous pests. In addition, the effectiveness of many entomophags considerably diminishes here because they exist at the expense of several close species of insects. This is why outbreaks of mass reproductions of pests are most frequent in agrobiocoenoses, and pesticides are used on a large scale to destroy them.

The perennial use of pesticides is direct action on biocoenoses and leads to the partial destroying of insect pollinators, ants, adversely affects fish, aqueous invertebrates, and birds. A side effect on animals and humans is observed.

The indirect influence of herbicides on the trophic and competitive relations between the members of an agrophytocoenosis is well known. They act indirectly on insects, destroying the plants they feed on (weeds) and changing the metabolism of the cultivated plants and weeds. After the use of herbicides, new amino acids not typical of normal metabolism are formed in plants, while some of them vanish completely. All this affects the fertility of the insects. For example, dalapon and TCA lead to an increase in the population of springtails and mites in the soil, while atrazine diminishes the number of click beetles and mites. Some herbicides are capable of producing partial sterilization of insects, and also of shifting the ratio of male and female specimens in the direction of a strong predomination of males. This is a property, for instance, of EPTC.

The use of herbicides also affects the development of pathogens of fungal diseases of plants. For example, the treatment of cabbage plantations with trifluralin lowers the infesting of the cabbage by clubroot.

Influence of Pesticides on Entomophags. The perishing of beneficial insects is the most noticeable when insecticides are used in forests and orchards because here these insects are represented by a large number of species and play an important role in controlling the size of pest populations. For example, as a result of overall aerial treatments of large areas of a forest with organochlorine insecticides to exterminate gypsy moths or pine loopers, the almost complete killing of the entomophags was observed. The mass extermination of burying beetles, European ground beetles, ichneu-

mon flies, carabids, wasp-flies, hover flies, tachina flies, and other beneficial species was observed. The number of entomophags after treatments was restored slowly because of the extermination of the biological objects on which they could accumulate. The danger of destroying populations of beneficial insects in the chemical treatment of large areas is considerably higher than when treating small areas where the replacement of the exterminated specimens is possible at the expense of migration from the adjacent sections. Of great significance are the periods of chemical treatment. Early treatment of a forest in the absence of a herbaceous soil covering appreciably lowers the danger to the entomophags. Of considerable significance are the residual amounts of poison in the forest after treatments, which can affect the biocoenosis of the forest for a long time. The degree of influence of a toxicant on entomophags depends on the consumption of a pesticide per unit area, the persistence of the substance, its form, the time of application, and the kind of treatment (overall or partial).

It has been found that the treatment of forests with aerosols of mineral and oil emulsions of HCH in strips causes little harm to the beneficial entomofauna, but ensures eradication of the pests.

The influence of pesticides on entomophags and acarophags in orchards is especially noticeable. The extermination of these insects upon the perennial use of organochlorine and organophosphorus insecticides may lead to the mass reproduction of harmful arthropods (insects and mites). For example, the increase in the population of the fruit-tree red spider mite when organochlorine pesticides are used is explained by the extermination of the predatory mites *Typhlodromus sp.* Outbreaks of mass reproduction of the wooly apple aphid after the use of the above insecticides are associated with the destroying of the parasite *Aphelinus mali Hald.* The mass reproduction of the cottony-cushion scale was noted after the extermination of its predator by organochlorine compounds.

The influence of insecticides on the beneficial entomophags in plantations of annual crops is less significant, although here too they are represented by a quite large number of species (up to 200-400). For example, it has been established that one hectare of a potato field may be inhabited by from 2000 to 3400 hover flies, from 2400 to 4800 carabids, and up to 203 000 predatory spiders, which perish almost completely upon the chemical control of the Colorado potato beetle.

Chemical treatments of wheat fields to combat pentatomids have a negative effect on the population of predators from the families *Carabidae* and *Coccinelidae.*

The spraying of fruit trees with sulphur compounds leads to the multiplication of the mussel scale because its parasite *Aphytis*

mytilaspidis and the predatory mite *Hemisar cortes malus* are exterminated. Sulphur exterminates typhlodromids, as a result of which the mass multiplication of spider mites occurs. Similar results may be obtained when using fungicides from the group of carbamates because in causing the mass extermination of typhlodromids, they create conditions for the development of the fruit-tree red spider mite.

The prevention of the mass multiplication of pests after the use of pesticides and the preservation of entomophags can be achieved in different ways. The expediency of using chemical means of controlling pests must be based on a thorough study of the crops and plantings and on prognosis in good time.

The optimal time for conducting treatments is the period when the entomophags are in a passive state or in places inaccessible for contact with the pesticide. For instance, in early spring treatments of an orchard, the pests wintering on the plants are killed, and no harm is caused to the beneficial insects that are in the soil at this time. The entomophags can also be preserved by carrying out selective treatments. In this case, a considerable part of the entomophags remain on the untreated part of the crops, in the orchards and forests. Great favour has been given to contour treatments of sugar beet crops against beet flea beetles, and of pea crops against pea beetles and weevils. It is also necessary to use insecticides with selective action (menazon, pirimicarb) which, while exterminating pests, have no harmful effect on their natural enemies.

Destruction of the entomofauna can be prevented by changing the ways and forms of using the insecticides. For example, by using systemic insecticides for the preplanting treatment of seeds, the contact of surface-dwelling entomophags with them is excluded, which prevents their extermination. The use of insecticides by spraying and in granules is less dangerous than by dusting. Of great significance in preventing the mass multiplication of pests is the combination of insecticides, especially when a collection of pests is being controlled, and some of them resist the action of individual pesticides.

Influence of Pesticides on Ants and Bees. The toxic action of pesticides on ants in the treatment of a forest depends on the kind of insecticide, the form and the dose of its application. For example, the treatment of a forest with a 25% mineral oil emulsion of HCH in a dose of 15 kg/ha affected the ants insignificantly. Only those specimens perished that came into direct contact with the pesticide during treatment or with the treated surface during the first day after the treatment.

In the overall treatment of a forest with pesticides, the self-protection of ants exhibits itself in their leaving the treated surface for their anthill.

Bees are killed most frequently when during treatment the pesticides are carried away onto areas with blossoming plants.

The danger of poisoning bees depends on the properties of the compounds. Stomach pesticides are very harmful to bees. They get into an insect's organism with nectare, pollen of the plants, or with water. The most dangerous among the contact insecticides are those penetrating through the chitin. The bee has the most developed nervous system of all insects, therefore it is the most sensitive to insecticides affecting the nervous system. Formulations based on polychloropinene or toxaphene have a low toxicity to bees.

Laboratory tests have shown the high stomach toxicity of carbaryl and trichlorphon to bees. The lethal dose of these pesticides is much smaller than the concentrations used for protecting plants. The contact action of carbaryl on bees is 9.8 times greater than that of trichlorphon. Carbaryl may cause the death of 90.4% of all bees and persist three or four days. Beauverin is also dangerous to bees. This biological formulation causes the death of bees in a rather long time after its application (three weeks).

In addition to the direct danger of the insecticides used, it must be borne in mind that these substances may appreciably weaken bees' organisms and promote their infection with bee pests. The toxic action of pesticides on bees depends on the periods and ways of application. Most fungicides and herbicides are only slightly or not dangerous to bees. The use of even the most toxic pesticides in the form of aerosols in the early spring in the absence of blossoming plants does not harm bees.

The main causes of the mass poisoning of bees by toxicants are the absence of strict planning of measures for the chemical protection of plants and the failure to observe the rule of giving 3-5 days' notice of treatment indicating the specific time, place, and nature of the scheduled chemical treatments of plantings of agricultural crops. It is dangerous to treat plants with poisonous chemicals in the daytime when the mass flight of bees takes place, and also to treat large bodies of entomophilic plants in the blossoming stage with pesticides having a prolonged residual action. Bees also become poisoned when the treated fields are directly adjacent to plantings of blossoming honey plants. The poisoning of bees is noted more frequently in aerial spraying at a wind velocity exceeding 2 m/s and a flying altitude of the plane over 5 m because of the large drift of the pesticide toward lands visited by bees.

With a view to the toxicity of pesticides to bees and the duration of its persistence, it is necessary to select the substances so that their residues will be completely decomposed before the plants blossom. The presence of pesticide residues on blossoming plants even in amounts not toxic to bees leads to their accumulation and concentration in the honey.

To protect bees from the action of pesticides, chemical treatment must be carried out in the evening or early morning. During the treatment, the bees must be isolated or removed elsewhere.

The isolation period depends on the features of the pesticide used. When employing a lime-sulphur concoction, sulphur, or blue vitriol, bees should be isolated during the period of treatment; when employing Bordeaux mixture, copper oxychloride, 2,4-D, toxaphene, folpet, tetradifon, monuron, fenuron, dalapon—up to 5-6 hours after treatment; when employing zineb, captan, simazine, nitrafen, chlorpropham, atrazine, polychloropinene—for one day; when employing malathion, parathion-methyl, menazon, trichlorometafos-3, barban, trichlorphon, DNOC, the bees should be isolated for 2 days.

If plants are being protected by using HCH, carbaryl, heptachlor, metasystox, dimethoate, the isolation period is increased to 3-4 days. In zones with a low temperature and an increased humidity of the air, the periods of isolation are increased by 1-2 days.

3.5. Action of Pesticides on Birds and Animals

Being biologically active substances, stable pesticides may negatively affect not only invertebrates, against which they are mainly used, but also warm-blooded animals (including birds).

Birds may perish when they peck disinfected seeds as a result of the careless handling of disinfected grain. Insectivorous birds may perish by feeding on poisoned insects.

When the environment is contaminated with pesticide residues, fish-eating and carnivorous birds at the end of the food chains may perish first of all.

Persistent organochlorine toxicants are the most dangerous to birds. When such pesticides get into a bird's organism, the reproduction process may be violated. The action on birds of other pesticides belonging to different classes of organic compounds is insignificant owing to their low toxicity and rapid detoxication in the environment. Studies performed in the USSR showed that upon chemical treatments, birds leave the territory being treated, while sometimes they die of poisoning because the established schedules and safety measures are violated in regions where pesticides are being used to control rodents, in zones of grain cultivation, and in the chemical treatment of orchards and forest areas.

In the chemical protection of plants, animals are in danger of being poisoned as a result of poisoning of their food or directly because of the action of toxicants.

The most dangerous properties of organochlorine insecticides include their negative action on the reproduction of animals and their secretion with milk. A decrease in the number of offspring in the litters of animals is noted, and also the death of young speci-

mens in test animals to whose food HCH was added in the doses used in field treatments. Organophosphorus compounds, the derivatives of carbamic acid and urea are less dangerous because they relatively rapidly metabolize in animal organisms to simple compounds.

Animals may develop protective reactions to toxicants, which makes it possible to avoid somewhat the harmful effect of pesticides. Animals are capable of choosing unpoisoned food because many pesticides have repellent properties for warm-blooded animals. Quite often, the migration of animals from treated areas is noted after the use of pesticides.

Protective reactions appear upon the action of pesticides not only in individual specimens, but also in a population as a whole. An increase in the number of females in a litter is one of the protective reactions (hares, rabbits, and some species of field-mice). Forms resistant to pesticides appear in warm-blooded animals, and they transmit their resistance to their progeny.

As a whole, the reasons why animals are poisoned and die often lie not in the toxic properties of pesticides, but in serious violation of the regulations and rules for chemical treatment.

3.6. Action of Pesticides on Plants Being Protected

Of major significance when using pesticides is their action on the plant being protected.

Different toxicants have a different physiological activity with respect to plants.

The varying resistance of plants to pesticides is determined by the chemical composition, doses, and formulation, the ways and periods of treatment, the growth stages, the anatomical and morphological structure of the plant, its organs and tissues.

The resistance of different species and kinds of plants to pesticides is based on their biochemical differences in metabolism and on the differences in their physiological reaction to these compounds.

It has been established that among plants there is no systematic group (class, family, genus) within which all the representatives would be identically resistant to pesticides. Even within a single species, individual varieties of plants may behave differently with respect to pesticides.

The different reaction of individual varieties of plants within a species to treatment with pesticides is confirmed by the results of numerous tests. For example, double interline hybrids of corn are considerably more resistant to the herbicide 2,4-D than simple hybrids or inbred lines. Variety differences in the treatment of plants with pesticides were discovered in potatoes, peas, flax, lupine, sugar beets, tobacco, and other crops.

Different varieties of fruits and berries vary considerably in their reaction to treatment with pesticides.

Local and General Action of Pesticides on Plants. Plant Burnings. The action of pesticides on plants begins from the instant of contact and penetration through the leaves, stems, or roots. Different pesticides behave differently. Most herbicides and insecticides with a systemic action, acaricides, and some fungicides penetrate into plants quite rapidly and are translocated in them, having a general action on the entire plant organism. Some pesticides are not capable of moving, and being localized at the spots of initial penetration, have a local action. When improperly used, pesticides may damage plants, causing burns (scorches) or the dying off of tissues.

The phytocidal action of pesticides depends directly on the content of the active ingredient, the solubility in water, and the chemical activity.

The burning action of pesticides is due to hydrogen ions in the working solution and depends on the degree of electrolytic dissociation of the compounds. In this connection, formulations must never contain a surplus amount of free mineral acids and acid salts. The unsaturated hydrocarbons and aromatic compounds contained in mineral oils are also dangerous to plants.

Inorganic substances soluble in water, for example copper (blue) vitriol, burn plants most frequently (and, consequently, are the most dangerous). This is why the vitriol is used with the addition of freshly slaked lime in the form of a Bordeaux mixture.

Pesticides only slightly soluble in water (copper oxychloride) may also cause burning. The explanation is that their solubility on the surface of plants increases sharply owing to the plants' excretions—carbon dioxide and water.

Burning may be caused by fungicides and organic insecticides.

The degree of burning of plants by pesticides depends on the environmental conditions and the specific features of the plants. Warm weather, as a rule, promotes the manifestation of a burning action. In the daytime, with increased gas exchange and with open stomas on the leaves, the burns may be stronger than at night, when the stomas are closed. Pesticides have a greater action on plants whose integument tissues are thinner. Plants growing in humid conditions are more liable to be burned.

Inorganic pesticides have a local burning action.

Features of Penetration, Movement, and Metabolism of Pesticides in Plants. Pesticides can readily penetrate into a plant through its roots, especially if preplanting treatment of the seeds was carried out, or the toxicants were incorporated into the soil. Pesticides penetrate into the roots notwithstanding the poor solubility of individual substances in water. This is associated with their solubility in lipids.

Pesticides are evidently absorbed by the roots in the same way as nutrient substances are, by diffusion, exchange adsorption, and active transfer of molecules and ions.

This process may be of a passive nature, when the pesticide ions and molecules adsorbed on the surface of the roots penetrate in an unchanged form into the free space of a cell and further move with the flow of water along the conducting vessels and cells of the green organ tissues. The pesticides may simultaneously enter a plant by metabolism when, being adsorbed on the outer surface of the cytoplasm of the roots' cells, they are immediately involved in intensive metabolism. As a result of biochemical reactions, the pesticides may be irreversibly decomposed or may form complexes with the components of a cell. The intensity of pesticide entry via the roots grows with an increase in the dose.

The movement of a pesticide from the soil solution into a plant depends on the properties of the soil. Clay and humous soils greatly adsorb pesticides, and in this connection the latter become less accessible to plants. The moisture content of the soil is of considerable importance. The intensive absorption by a plant of insecticides from the soil in conditions of adequate moisture is closely related to the vigorous inflow and movement of water and nutrient substances.

In the treatment of growing plants, the pesticides penetrate into them mainly through the leaves (cuticle and stoma) in the form of a liquid or vapour.

Penetration through the cuticle depends in many aspects on the anatomic and morphological features of the integument tissues.

According to modern notions, the cuticle consists of the following four unevenly distributed components: (1) cutin—polymerized high-molecular acids and alcohols having simultaneously hydrophilic and lipophilic properties; (2) cuticular hydrophobic waxes—low-molecular ethers of fatty acids and monatomic alcohols of the fatty series with a short chain; (3) pectin—a hydrophobic substance of an amorphous structure permeable to water and polar compounds; and (4) cellulose—a hydrophilic substance with a fibrous structure having a high tensile strength.

The cuticle covers the entire surface of a leaf and the substomatic chamber (the surface of the mesophyllous and palisade cells inside a leaf open to the access of air) in the form of a solid film and is the main obstacle preventing the penetration of pesticides into the leaf. It is characterized by a negative charge and can adsorb water. The cuticle has a lipoid matrix, and lipophilic substances can penetrate through it. The ectodesmae of the cuticle are one of the possible ways for the penetration of hydrophilic compounds.

Pesticides penetrate into a plant through its leaves only if they are in the form of a solution or emulsion. After crystallization, no penetration of the substances takes place.

Several ways are known in which substances can penetrate into the protoplast of a leaf: polar (aqueous), non-polar (lipoid), and also in a combined way.

Hydrophilic pesticides can enter via the aqueous phase of the cuticle first into the acid components of the cutin, and then into the pectin and water-permeable cytoplasmic membrane. In conditions of an increased humidity, the micropores of the cuticle and cutin are saturated with water. In this case, the drops of pesticide getting onto the leaf contact with its aqueous phase, begin to penetrate into the apoplast and are further absorbed by the symplast. With insufficient moisture, the micropores of the cuticle are filled with air, and the drops of the pesticide solution, encountering air locks in the pores, cannot come into contact with the water in them. In this case, the aqueous way of penetration is greatly hampered.

When there is insufficient moisture in a plant, pesticides penetrate into it in the lipoid way. Lipophilic substances penetrate through the fat components of the cell membrane. A thin adsorption layer of liquid forms on the hydrophobic components of the cuticle and the membrane of the cell.

Many pesticides, having simultaneously polar and non-polar properties, can move along the phase interface.

The penetration of pesticides through the cuticle is determined by their solubility in water or in separate components of the cuticle and cell membrane and depends on the degree of their polarity. The cuticle is well permeable to oils, therefore many pesticides soluble in an oil readily penetrate through it. Having passed through the cuticle and cuticular layers, the pesticide molecules encounter an obstacle along their path to the protoplast in the form of the cellulose layers of the cell membrane. Pesticides penetrate through a cell membrane by diffusion through the interfibrillar spaces and ectodesmae and are absorbed by the plasmalemma. Owing to special properties of the membranes and to desorption or pynnocytose, the absorbed molecules of the pesticides are desorbed into the cytoplasma. This is a metabolic process, and breathing or photosynthesis supplies the energy needed to activate absorption. Pesticides also penetrate into a leaf via the stomas. Large open stomas can easily transmit the vapours of pesticides from solutions sprayed onto the plants, and also aqueous and oil solutions and emulsions of pesticides with a low surface tension.

Pesticides may also enter a plant directly through the epidermis, bark, and integument tissues of its stem.

The pesticides absorbed by a plant can move in it along the phloem, ray parenchyma, cell walls, along the xylem with the transpiration flow, and along the intercellular spaces.

Many pesticides that penetrate into a leaf move along the phloem. Pesticides dissolved in oils move in plants owing to the capillary

flow along the micropores of the cell walls. The vapours of volatile pesticides move along the intercellular spaces of a plant.

Pesticides move mainly into the rapidly growing parts of a plant, and their translocation rate varies. HCH, heptachlor, organophosphorus pesticides, many herbicides, and also some fungicides move quite rapidly along the vascular system of plants. The translocation rate of pesticides in a plant coincides with that of the endogenic substances along the phloem and xylem.

Pesticides undergo metabolism in plants under the action of enzyme systems.

The rate of metabolism of pesticides varies (from 7-8 to 15-20 days) and depends on the properties of the substance, and also on the specific and age features of the plants. This process is faster in younger plants than in old ones, the explanation being the higher physiological activity of the former. Synthetic processes predominate in young tissues in connection with the increased meristematic activity in them. Young tissues also have a higher content of biocatalysts and substances with a high physiological activity (enzymes, hormones, vitamins). The active form of these compounds reacts with a pesticide, causing it to change. Old tissues do not have such favourable conditions for changing a pesticide because here hydrolytic processes associated with the decomposition of organic compounds and the formation of the simplest low-molecular compounds predominate.

Various pesticides metabolize in plants in different ways with the formation of decomposition products in the long run. A substance must not necessarily metabolize in one strictly definite way in plants. On the contrary, the same compound may be involved in different reactions leading to the formation of a multitude of diverse products of metabolism.

Comparative Toxicity of Pesticides to Target Organisms and Plants Being Protected. The comparative toxicity of pesticides to the target organisms and the plants being protected is characterized by the chemotherapeutic coefficient expressed by the ratio of the minimum dose of a pesticide killing the target organism to the maximum dose endured by the plant being protected:

$$C_{ct} = \frac{D_1}{D_2}$$

where C_{ct} = chemotherapeutic coefficient
D_1 = minimum dose of a pesticide at which the target organism is killed
D_2 = maximum dose of the pesticide endured by the plant being protected.

The phytotoxicity of herbicide formulations is compared by using the relative activity (A_{rel}) showing how many times the phytoto-

xicity of one formulation is larger or smaller than that of another one taken as the reference formulation:

$$A_{rel} = \frac{ED_{50} \text{ of formulation being tested}}{ED_{50} \text{ of reference formulation}}$$

An essential condition for establishing the relative activity of formulations is their comparison in doses yielding the same effect (in the given case, ED_{50}) because a double effect is not ensured by a double dose. For example, in studying the effectiveness of different specimens of the herbicide 2,4-D, it was established that an identical effect (a 50% reduction of the harvest of mustard) was achieved by applying 0.4 kg of the first specimen, 0.5 kg of the second specimen, and 0.6 kg of the third specimen per hectare. A comparison of these doses reveals that to obtain the same effect, it was necessary to apply 1.5 times more of the third specimen and 1.2 times more of the second specimen than the amount of the first one.

The selectivity of herbicide action is characterized by the selectivity parameter and the selectivity index.

The selectivity parameter (P_{sel}) is the ratio of the phytotoxicity indices of one formulation for different species of plants. It shows how many times the toxicity of the formulation is higher for one species of plants than for another one:

$$P_{sel} = \frac{ED_{50} \text{ of first plant}}{ED_{50} \text{ of second plant}}$$

Of the two plants being compared, the one with the higher ED_{50} value is taken as the first one. For this reason, herbicides with a higher selectivity parameter have a higher selectivity.

The selectivity index (I_{sel}) is the ratio of the dose causing a small drop in the yield to the dose killing most weeds, i.e. it shows how many times the dose causing a considerable decrease in the weediness is less than that having a toxic action on the cultural plants. A pesticide may be considered to have an adequate selectivity if while destroying at least 80% of the weeds, it does not affect or only slightly suppresses (within 20%) the cultural plants.

The ratio of the doses causing a 20% drop in the yield of the cultural plants and an 80% killing of the weeds is conventionally taken as unity. Consequently, the higher the value of the selectivity index, the higher is the selectivity of the herbicide. The selectivity index allows us to compare the selectivities of different herbicides.

An example of a high selectivity is the use of propazine for controlling carrot weeds. In this case, 80% of the weeds are killed already at a dose of 0.92 kg/ha, while depression of the carrots (a 20% drop in the yield) is observed only at a dose of 2.8 kg/ha, which is more than three times larger than the first dose. The selectivity index for propazine in this case will be $2.8 : 0.92 = 3.04$.

3.7. Integrated Systems of Plant Protection— the Basis for Preventing the Harmful Action of Pesticides on the Environment

An important role in eliminating the harmful action of chemical means of plant protection on the environment is assigned to the rational application of pesticides in integrated plant protecting systems. The latter are based on the greatest possible utilization of environmental factors causing harmful organisms to perish or limiting their vital activity. The main task of such systems is keeping the number of harmful insects at a level when they do not cause perceptible harm by using a collection of measures instead of a single one.

The Soviet entomologists A. Znamensky, V. Shchegolev, and others in 1930-1932 developed the theoretical prerequisites of a system of measures including a collection of agrotechnical procedures, chemical, biological, and other ways of controlling pests. This course, supplemented by such a concept as the criteria determining the need of using chemical treatments, has received general acknowledgement at present under the name of an integrated system.

A system of antismut measures was developed and implemented in the USSR. Its result was a reduction in the losses of the grain crop due to smut from 10-30% to 0.01-0.02% during two or three years. The use of an integrated system made it possible to suppress the mass reproduction of locusts. Systems of measure to control grapevine mildew, cotton wilt, pasmo, tobacco blue mould, beet weevils, and spider mites on cotton markedly lowered the losses of the crop.

With a view to the chemical method being the leading one, exceedingly great attention is given to its improvement.

The fundamental principle of rational chemical pest control consists in taking complete account of the ecological situation on agricultural lands, having an exact knowledge of the criteria of the strength of the harmful species, and also of the number of beneficial organisms suppressing the development of the pests.

There are four main ways of improving the safety of the chemical method of protecting plants.

1. Improving the assortment of pesticides with the aim of diminishing their toxicity to humans and beneficial animals, lowering their persistence, and increasing their selectivity.

2. Using optimal ways of pesticide application such as preplanting treatment of seeds (which eliminates early spring and late autumn treatments in orchards), band or strip treatments, and the use of granulated formulations.

3. Optimizing the use of pesticides with a view to the economical expediency and necessity of employing pesticides for suppressing populations (with account taken of the economical threshold of harm for each species of pest in a zonal aspect).

4. The strictest regulation of the use of pesticides in agriculture and other branches on the basis of a comprehensive study of their sanitary and hygienic characteristics and the conditions for ensuring safety when working with them (Yu. Fadeev, 1975).

At present, compounds that are highly toxic and persistent in nature are being replaced with ones having a lower toxicity and persistence.

To preserve beneficial insects, highly selective pesticides must be used for chemical treatment that are poisonous only to definite targets and are not a hazard to the natural enemies of the pests. Among them are tetrachlorvinphos, phosalone, and DAEP. Fungicides are virtually harmless to beneficial insects. An important way of improving the selectivity of pesticides having a broad spectrum of action is the rationalization of the ways of applying them with a view to the economical threshold of harmfulness for each pest species. This makes it possible to reduce the area or number of chemical treatments with no harm to the culture being protected. For example, in Tajikistan (a Soviet republic in Central Asia), the chemical method must be used when 8-12 bollworms are detected per 100 plants of cotton of type 108-f grades, and 3-4 bollworms for fine-staple grades. It is sufficient to carry out selective treatments using pesticides having a definite selectivity with respect to bollworms and mites (dicofol, dinobuton, phosalone, milbex).

Chemical measures for controlling beet leaf miners on beet plantations are justified if 8-10 eggs are detected on an average on one plant in the stage of four leaves, 12-14 eggs in the stage of six leaves, and 22-25 eggs in the stage of eight leaves.

When using insecticides, it is the safest to employ systemic substances, especially in the treatment of seeds, or the incorporation of granulated formulations into the soil when or after planting. An important advantage of using systemic insecticides when planting is the prolonged protection of the plants in the most vulnerable stage of their development when the seeds and seedlings may be destroyed very easily or greatly damaged by pests.

Systemic and some contact (heptachlor) granulated insecticides effectively protect the seeds and seedlings of various cultures from pests dwelling in the soil (click beetles, larvae of dor bugs, etc.), from insects inside the plants (the larvae or maggots of cabbage, onion, carrot rust-flies, Hessian, winter, and frit flies) and on their surface from sucking pests (aphids, mites). The incorporation into the soil of fertilizers with pesticides when planting not only combines two operations, but also facilitates an increase in the crop. For example, the twofold sowing and postemergence application of granulated superphosphate with dimethoate to control cutworms increased the yield of cotton by 500 kilograms per hectare. Low volume spraying and ultra low volume spraying are the most productive

and make it possible to complete treatments in a very short time before the pests manage to cause significant harm. In a number of parameters, evening and especially night spraying is very promising first of all for orchards and blossoming alfalfa. Nights are usually windless, which noticeably diminishes the danger of drift, and improves the settling and uniform covering of the plants with the pesticide. At night, some pests are more active (cutworms, mosquitoes, etc.), which ensures a greater contact with the pesticide.

The majority of entomophags, especially predators, are the most resistant to the action of insecticides in their inactive phases of development (eggs, pupae). In this connection, the most acceptable are early spring and autumn eradicating treatments. Of great importance for the preservation of entomophags and acariphags is the selective use of pesticides at the beginning of a growth in the number of pests in isolated locations. Alternating band treatment when strips treated with a pesticide alternate with untreated ones gives the greatest effect in combatting forest pests.

Boundary treatments of fields are rational with respect to pests that migrate in the spring from the sites where they wintered to crops. Here pesticides and labour are saved, and the beneficial insects (at the middle of the field) are preserved.

It is most promising to control mites and insects that have developed resistance to certain pesticides by alternating pesticides from different classes with a different mechanism of action.

To prevent contamination of the soil with pesticide residues, the incorporation of persistent pesticides into the soil must be limited as much as possible, while where necessary, rapidly decomposing substances should be placed into the drill rows, holes, and hollows (locally), which reduces the consumption of the pesticide.

Persistent substances must be used in the conditions of multiple crop rotation, where the rotation of the crops is attended by alternation of various pesticides, thus preventing their accumulation in the soil. Organophosphorus compounds and dilor may be used to treat plants on the same field every year. Heptachlor, technical HCH, and carbaryl should be used every other year. Polychloropinene and toxaphene should be used once in four or five years, i.e. to treat not over two fields in a 9-10-field crop rotation. During a single season, it is good practice to use different pesticides, even if they are similar in their spectrum of action, so that they will be able to decompose as much as possible during the vegetative season.

The employment of toxicant rotation with the observation of two or three year intervals between repetitions of the same pesticides or the alternation of different ones during one season is an essential condition for the organization of the chemical protection of plants in perennial plantings, and also in specialized farms with a high degree of rotation of the same crop.

Chapter 4

SANITARY FUNDAMENTALS OF PESTICIDE APPLICATION

The pesticides used for protecting plants are biologically active substances and act not only on their targets, but are also a potential hazard for nature and the health of humans.

Pesticides are characterized by a different toxicity to humans and warm-blooded animals. Their action manifests itself not only directly during the period of application, but may also be chronic. Some of them, accumulating on objects of the environment, gradually concentrate in the food and fodder, become a real hazard to beneficial animals and to humans, and may lead to serious alterations in the ecosystems, biocoenoses, and landscapes.

The actual danger of a pesticide cannot be appraised only according to its toxicity characteristics. The contamination of the environment by pesticides cannot be prevented by purification facilities and trapping devices. Enormous areas of agricultural lands and hundreds of thousands of tonnes of products are treated with pesticides; consequently, they continuously circulate in the habitat of humans. Residues of pesticides are detected in the air, water, soil, and in plant and animal organisms. This is why the chemicals used in agriculture must be studied from a general sanitary standpoint, with a view to their behaviour in the environment and to all the sources from which they may enter a human organism.

The main task in ensuring safety in pesticide application is the finding of effective measures and means for the sanitary protection of the environment, especially of the atmospheric air, food products of a vegetable and animal origin, sources of water supply, and the soil, from contamination with chemicals in amounts dangerous for the health of people. In establishing the sources and reasons of pesticide penetration into the environment and in determining their amount, hygienists predict the potential and actual danger of a definite substance, and develop ways and means of preventing poisoning.

Research into the hygiene of using pesticides is conducted by many scientific research institutes and sanitary epidemic stations of the USSR. This work is supervised and coordinated by the All-Union Scientific Research Institute of the Hygiene and Toxicology of Pesticides, Polymers and Plastics (VNIIGINTOKS).

Not a single chemical is used in agriculture without first being thoroughly studied by the relevant research institutions and without the permission of the USSR Ministry of Health.

Strict observance of the regulations in force and of the rules for the storage, transportation, and application of pesticides ensures

not only their effective action, but also safety to humans and beneficial animals, and prevents their accumulation in food products and the environment.

Causes of and Conditions for Poisoning by Pesticides. Humans and animals may be poisoned either by the pesticides themselves or by the products of their metabolism. Poisoning by pesticides may be occupational or encountered in everyday life.

Occupational poisoning occurs among workers busy in preparing the working formulations of pesticides or treating orchards or fields, or occupied in the treatment of seeds. Poisoning sometimes occurred upon the accidental spraying of pesticides when the apparatus was being prepared.

Cases are known of poisoning when drinking water, eating, or smoking during work with toxicants.

Cases have been noted of intoxication when caring for plants (weeding, trimming, etc.) soon after the application of pesticides. In the majority of cases, the cause of occupational poisoning was the performing of the work without the appropriate individual means of protection.

To prevent occupational poisoning, it is necessary to strictly observe the sanitary rules for working with, storing, and transporting pesticides, to use properly selected individual means of protection, and observe the quarantine periods before working on treated fields.

The poisoning by pesticides of persons having no direct relation to work with them is referred to as non-occupational poisoning. A major cause of such poisoning is the careless storage of pesticides. A great hazard to health is the use of containers freed of toxicants to store food products. Poisoning often occurs upon the unskilful use of pesticides to control synanthropic insects.

To prevent non-occupational poisoning, it is necessary to strictly control the use, storage, and transportation of toxic chemicals, and eliminate all possible ways of contaminating the environment with pesticides.

Of special importance is the protection of warm-blooded animals from being poisoned by pesticides. This is important not only to preserve beneficial animals, but also to eliminate a possible source of supplying pesticides into human organisms with products of an animal origin.

The poisoning of animals and the accumulation of residual amounts of toxicants in their organisms occur because of the improper use of chemical means of protecting cattle from insects, when the animals feed on plants containing pesticide residues or on treated grain, when water from contaminated sources is used, when fodder is given to them in containers emptied of toxic chemicals, or upon the accidental contact of animals with such chemicals.

A danger of poisoning birds and fish appears when persistent pesticides are used and the rules for the application, storage and transportation of toxicants are violated, when contact of the birds and fish with a poison scattered or washed into water basins is possible.

The systematic use of pesticides having cumulative properties leads to their concentration in the organisms serving as food for birds and fish.

All this points to the need of strictly observing the rules of personal and public safety when using pesticides.

The action of pesticides on warm-blooded animals and humans depends on many factors and is determined mainly by the chemical nature of the active ingredient, its dose, the duration of action, and the general state of the organism.

Upon penetrating into an organism, pesticides rapidly spread in it, becoming selectively accumulated in separate parts or organs of a body. Some of them are bound by proteins or other components of the cells, while others are metabolized and excreted from the organism.

Organophosphorus compounds, carbamic acid derivatives (carbaryl), and aromatic nitrocompounds (DNOC) are detected in various tissues of an organism already in a few minutes after ingestion. The maximum concentrations of these pesticides in the internal tissues is noted in one-half to six hours after entry. When ingested one time in a dose of LD_{50}, they are completely excreted from the organism in 24 to 96 hours.

Organochlorine compounds accumulate more slowly, and their maximum concentration is observed in 25 days or more after entry.

In large amounts, pesticides accumulate in the liver, kidneys, and heart. Most of them in small amounts penetrate into the brain.

The deposition of pesticides in some tissues is possible. For example, organochlorine compounds accumulate in fatty tissue. Some pesticides may accumulate in the skin and thence enter the blood. At the places of their accumulation, pesticides undergo metabolism with subsequent deactivation or activation.

Processes of metabolism occur most actively in the liver, kidneys, and also in the intestinal tissues. Metabolism is often the basic process lowering the concentration of a pesticide in organs. For instance, the concentration of heptachlor in the liver and fatty tissue mainly diminishes owing to its decomposition to epoxide and other metabolites.

Poisons are excreted from an organism via the kidneys, gastrointestinal tract, lungs, skin, or mammary glands.

The mechanism of the toxic action of pesticides is determined by the absorption, transportation, metabolism, and influence thereof on the general metabolism in an organism. The initial causes of the

toxic action of pesticides vary. Some pesticides cause a change in the cellular structures (for example, of the mitochondria), violating the conjugation of vitally important processes such as oxidation and phosphorylation of a substance.

Pesticides characterized by structural similarity to natural compounds of the organism join the conventional metabolism, as a result of which the functions of the metabolites synthesized with their participation are disrupted. For instance, the structural similarity of triazine derivatives to pyrimidine bases allows them to participate in metabolism as antimetabolites of pyrimidine bases, which leads to the synthesis of improperly built proteins. For this reason, the harmful action of triazine manifests itself when the new proteins begin to function. The ability of pesticides to react with active groups of enzymes leads to inactivation of the latter and causes violation of the exchange reactions in which they participate. The result is the accumulation of intermediate products of metabolism causing poisoning of the organism. Most organophosphorus pesticides are inhibitors of the cholinesterase activity of enzymes.

Just as diverse as the nature of pesticide action on the organisms of warm-blooded animals is the manifestation of this action. Pesticides cause acute, subacute, or chronic poisoning, affecting important organs and systems of an organism, disrupting exchange processes, and aggravating the course of previous diseases.

Pesticides may have a local action, destroying a tissue directly in the zone of contact of an organism with the poison. It may be irritative, anesthetizing, or necrotizing. The mucous membranes and lung tissue are especially sensitive to pesticides. Upon entering the blood, the pesticides are carried to different organs and tissues and affect the indices of an organism's vital activity. Under the influence of many pesticides, the gene responsible for the synthesis of hemoglobin is activated, changes occur in the morphological composition of the blood and the functional properties of the leucocytes, and shifts are noted in the content of the blood's erythrocytes.

Organochlorine insecticides act on the central nervous system, block a number of breathing enzymes, and disrupt the functions of the liver, kidneys, and other organs.

Carbamic acid derivatives act directly on choline receptors, inhibit the consumption of oxygen by tissues, cause depression of cholinesterase, and lower the activity of sulphhydryl enzymes and the enzymes of carbohydrate and oxidizing exchange.

Mercury-containing pesticides cause disorder of the central and peripheric nervous system, the gastro-intestinal tract, and disrupt the activity of the liver, kidneys, and the cardiovascular system.

Some pesticides call forth skin diseases (dermatitis, eczemas, urticaria), or act on the respiratory organs.

It has been established that certain pesticides may stimulate the formation of tumours, including malignant ones, cause mutations, violate the development of the fetus and the process of fertilization.

The studying of the mechanism of pesticide action on humans and warm-blooded animals and the determination of the main links affected by a toxicant set up the foundation for a directed search for substances that could be used as antidotes weakening the toxic action of pesticides and for healing persons subjected to the action of a toxicant. Such substances have been found and are being used very effectively. For example, upon poisoning by pesticides from among the group of organophosphorus compounds, cholinesterase reactivators are used such as dipyroxim (TMB-4).

Unithiol is used as an antidote against poisoning by toxicants that act on the sulphhydril groups of natural compounds.

4.1. Sanitary Classification of Pesticides

A sanitary classification makes it possible to give a comparative characteristic of various pesticides and determine what pathological effect is of the greatest danger when using a given substance.

Depending on their toxicity and degree of danger, pesticides as regards their main criteria are divided into a number of categories or groups.

I. *According to their toxicity when ingested into the stomachs* of test animals (rats) (**oral toxicity**).

1. Powerful toxicants—LD_{50} up to 50 mg/kg.
2. Highly toxic substances—LD_{50} equals 50-200 mg/kg.
3. Moderately toxic substances—LD_{50} equals 200-1000 mg/kg.
4. Slightly toxic substances—LD_{50} over 1000 mg/kg.

Following this classification, the pesticides recommended for use in agriculture are divided into the following groups.

Group 1. Powerful toxicants: antu, chloropicrin, diphacinone, ethylmercury chloride, gliftor, mercurbenzene, mercurhexan, methyl bromide, warfarin, zinc phosphide.

Group 2. Highly toxic substances: diazinon, dichloroethane and its distillation residues, dichlorvos, dimethoate, dinobuton, DNOC, endosulfan, "gamma" smoke pots, heptachlor, hexachlorobutadiene, lindane technical and a 50% wettable powder, metasystox, parathion-methyl, phenthoate, phosalone, phosmet, sodium pentachlorophenolate.

Group 3. Moderately toxic substances: actril AS, actril M, barban, binapacryl, blue vitriol, butyl captax + magnesium chlorate, calcium cyanamide, cambilene, carbaryl, chlorthiamid, copper oxychloride, copper trichlorophenolate, cuprosan, cyanophos, 2,4-D butyl ester, 2,4-D crotyl ester, DAEP, dazomet, D-D, DDB-

technical, DEF, dicofol, dimethoate granules, diquat, FDN, fenitrothion, fenthion, fenthiuram, fenthiuram molybdate, formalin, formothion, fosfaman, gammahexane, HCH (technical, 12% dust, 25% powder on phosphorus flour), hexathiuram, lindane (granulated 4% and 2% fine-grained, granulated 2% coarse-grained, 16% emulsifiable concentrate), malathion, MCPA, MCPP, metaldehyde, metam-sodium, methallyl chloride, miltox special, nitrafen, pebulate, phytobacteriomycin, phenmedipham, polychloropinene, polychom, propachlor, pyrazophos, rodan, 2,3,6-TBA, thiram, tigam, toxaphene, trichlorfon, trichlorol-5, trichlorometafos-3.

Group 4. Slightly toxic substances: agelon, anilat, arenarin, atrazine, aziprotryne, banlen, banvel D, beauverin, benomyl, Bordeaux mixture, bromophos, bromopropylate, calcium chloride, captan, carboxin, chloramben, chlorbromuron, chloroxuron, chlorpropham, chlorthal-dimethyl, copper naphthenates, cuprozin-1, cycloate, 2,4-D amine salt, 2,4-D low-volatile esters, 2,4-D octyl ester, dalapon, 2,4-DB, desmetryne, dialen, diamet-D, dicamba, dichloralurea, dichlofluamid, dilor, dinocap, diphenamid, diuron, dodine, entobacterin, EPTC, fenuron, fluometuron, folpet, formulations No. 30, 30A, 30M, 30S, 30SS, green soap, green vitriol, hexachlorobenzene, lenacil, lime sulphur, linuron, lumeton, magnesium chlorate, menazon, metiram, metobromuron, metoxuron, meturin, milbex, molinate, monolinuron, monuron, nitrofor, norea, oxadiazon, oxine-copper, pentanochlor, petroleum oils, picloram, polymarzin, polytriazine, prometryne, propanil, propazine, pyrazon, quintozene, simazine, sodium TCA, sulphur (colloidal, wettable powder, ground, and lump), tetrachlorvinophos, tetradifon, thiophanate-methyl, triallate, trifluralin, zineb.

Pesticides relating to powerful toxicants and highly toxic substances are a great hazard because of their ability to cause acute poisoning. To predict the danger of acute poisoning, the zone of toxic action of a pesticide is determined from the ratio of the median lethal dose (LD_{50}) to the threshold dose. When this ratio is small, the zone of toxic action is narrow, and the danger of acute poisoning is great.

The use of powerful toxicants and highly toxic substances is diminishing with every passing year. The assortment of pesticides in 1979 contained 20% of powerful toxicants and toxic substances, while in the nearest future their amount will diminish to 5%.

Work with pesticides of the first group is performed by a constant staff; the procedure of obtaining, transporting, storing, and keeping accounts of them is regulated by special instructions. It is prohibited to use powerful toxicants and highly toxic substances for the treatment of parks and green plantings within the confines of populated localities and on household plots. Food products containing residues of pesticides belonging to powerful toxicants and

highly toxic substances in amounts exceeding the tolerance levels may not be used as food. An exception are food products that are used only after heat treatment that completely decomposes these pesticides.

II. *According to their toxicity in entering through the skin* (**dermal toxicity**).

1. Acute—LD_{50} below 300 mg per kg, the skin-oral coefficient is less than 1.
2. Pronounced—LD_{50} equals 300-1000 mg per kg, the skin-oral coefficient is 1-3.
3. Slightly expressed—LD_{50} over 1000 mg per kg, the skin-oral coefficient is over 3.

The skin-oral coefficient is defined to be the ratio of the value of LD_{50} determined when a substance is applied to the skin to the value of LD_{50} when it is introduced orally into the stomach. For example, if LD_{50} when entering through the skin is 300 mg per kg, and when introduced orally is 400 mg per kg, the skin-oral coefficient will be $300 : 400 = 0.75$. The higher the value of this coefficient, the smaller is the danger of poisoning when the relevant substance gets onto the skin.

Pesticides characterized by acute dermal toxicity such as DEF, bromophos, endosulfan, and dichlorvos are especially dangerous. Reliable means for protecting the skin are needed when working with them.

When choosing pesticides having the same oral toxicity, preference should be given to those having a lower dermal toxicity.

III. *According to the degree of volatility.*

1. A very dangerous substance—the saturating concentration is larger or equal to the toxic one.
2. A dangerous substance—the saturating concentration is larger than the threshold one.
3. A slightly dangerous substance—the saturating concentration has no threshold action.

Substances having a high volatility penetrate into an organism through the respiratory organs and are characterized by an inhalation toxicity.

Pesticides used for fumigation and mercury-containing substances for the treatment of seeds are very dangerous. When working with them, one must reliably protect the respiratory organs, using gas masks with the corresponding filter.

IV. *According to cumulation* (**chronic toxicity**).

1. Substances having supercumulation—the cumulation coefficient is less than 1.
2. Pronounced cumulation—the cumulation coefficient is 1-3.
3. Moderate cumulation—the coefficient is 3-5.
4. Slightly expressed cumulation—the coefficient is over 5.

By cumulation is meant the accumulation of a poison in an organism as a result of incomplete detoxication and excretion from the organism or an increase in the effect of its action.

Material and functional cumulation are distinguished. Material cumulation is the name given to the accumulation of a toxic substance in an organism as a result of repeated contacts. The ability of material cumulation is a property of many pesticides from among the group of organochlorine compounds and of mercury pesticides.

Functional cumulation signifies not accumulation of a poison, but summation of the effect of its action. Certain organophosphorus compounds (parathion-methyl, malathion) have such a property.

The existence and magnitude of the cumulative action are determined in tests on animals by repeatedly treating them with various doses of pesticides. The magnitude of cumulation is characterized by the coefficient of cumulation C_{cum} determined by the ratio of the summary median lethal dose of a substance when introduced repeatedly to the median lethal dose when used once:

$$C_{cum} = \frac{LD_{50} \text{ (in chronic test)}}{LD_{50} \text{ (in single test)}}$$

When the coefficient of cumulation is lower, the cumulative action of the relevant pesticide is more pronounced.

Supercumulation and pronounced cumulative action are properties of pesticides exhibiting a high persistence in biological media that are capable of circulating in food chains and of gradually accumulating in organisms. They include many substances from among the group of organochlorine compounds (HCH, etc.).

V. *According to the persistence* (in the soil).

1. Very persistent substances—the time needed for decomposition into non-toxic components exceeds two years.

2. Persistent substances—the time needed for decomposition into non-toxic substances is 0.5-2 years.

3. Moderately persistent substances—the time needed for decomposition is 1-6 months.

4. Slightly persistant substances decomposing into non-toxic components within a month's time.

Very persistent substances must never be used in agriculture. Persistent substances include pesticides having a negligible volatility that do not change chemically under the influence of atmospheric factors. Among them are simazine, monuron, thiram, mineral oils, and DNOC.

Substances having a comparatively low volatility and slowly changing their chemical properties such as HCH, malathion, trichlorfon, dimethoate, zineb, metam-sodium, and esters of 2,4-D belong to the group of moderately persistent pesticides.

Pesticides subject to considerable evaporation and chemical changes under the influence of the environment relate to the group of slightly persistent substances. They include fumigants, mercury formulations, and parathion-methyl dust. They have to be stored in sealed containers.

In addition to the basic criteria listed above that make it possible to give a sanitary appraisal of pesticides, other pathological effects of their action are studied such as blastomogenesis, mutagenesis, teratogenesis, and embryotropism.

Blastomogenesis characterizes the ability of pesticides to cause the formation of tumours. If a tumour is malignant, the pesticide is said to be a carcinogen.

With respect to their ability to cause the formation of tumours, pesticides are divided into clearly carcinogenic substances producing cancer in humans, strong carcinogens in tests on animals, cancerogens—substances producing tumours in animals (their action on humans has not been established), and slightly carcinogenic substances—weak carcinogens in tests on animals.

The **mutagenesis** of pesticides is characterized by the frequency of appearance of mutations in plants, animals, and the drosophile. Five groups of pesticides are distinguished according to this feature: supermutagens—substances causing 100% of mutations in plants and animals (100 mutations on 100 chromosomes are taken as 100%); strong mutagens—substances producing 5-10% of mutations in the drosophile; moderate mutagens causing 2-5% of mutations in the drosophile; weak mutagens causing 1-2% of mutations in the drosophile; and very weak mutagens causing 0.5-1.0% of mutations in the drosophile.

The ability of pesticides to cause the appearance of monstrous or abnormal offspring is characterized as **teratogenesis.** There are distinguished obvious teratogens—pesticides causing abnormalities in humans, reproduced experimentally in animals, and those suspected of being teratogenic—pesticides producing abnormalities in test animals.

Embryotropism is the property of pesticides to violate the normal development of an embryon. Selective and moderate embryotropism are distinguished. The former is characterized by the absence of toxicity to the maternal organism. Moderate embryotropism manifests itself together with other toxic effects.

It has been established during recent years that some pesticides have allergenic properties. They cause a change in the reaction of organisms to repeated treatments. When such substances act for the first time, protein antibodies form in an organism as a result of a protective reaction. A changed reaction of an organism consists in lowering or more often increasing the sensitivity of the organism to the given allergen, and an allergenic effect may tell at very small

doses. For example, the first application to the skin of thiram (1000-2000 mg/kg) did not cause an irritative action, while upon the repeated application of thiram (50 mg/kg) to the test object sharp hyperemia was noted. A variant of allergy is idiosyncrasy associated with an increased individual sensitivity of an organism to certain substances. It manifests itself in reddening of the mucous membranes, in the appearance of edemas, rashes, itching and burning of the skin. There are distinguished strong allergens causing an allergic state in most people even when acting in small doses, and weak allergens producing an allergic state in a few individuals.

The sanitary classifications make it possible to appraise pesticides comprehensively. If a pesticide with respect to one of the parameters relates to the first group of the sanitary classification, it is very dangerous to humans and warm-blooded animals and must never be used in agriculture.

Pesticides must meet the following sanitary requirements:

(1) substances having a low toxicity to warm-blooded animals and humans must be used in agriculture;

(2) persistent substances that do not decompose in natural conditions into non-toxic components in the course of two or more years must never be used;

(3) it is prohibited to use substances with sharply expressed cumulation;

(4) substances must not be used if preliminary studies of them has established the real danger of their being carcinogenic, mutagenic, embryotoxic, or allergenic.

With the discovery of new toxicological and sanitary properties of pesticides and the development of more accurate and reliable methods of studying them, the sanitary classification will be expanded and improved.

4.2. Rules for Using Pesticides

The toxicity of pesticides to humans, and their ability to remain in the environment and accumulate in the products obtained require the establishment of strict scientifically substantiated recommendations, norms, and restrictions (regulations) for each substance ensuring their effective and safe application.

Rules for using pesticides are worked out by the USSR Ministry of Agriculture together with the USSR Ministry of Health.

Every year there is issued an approved "List of Chemical and Biological Means for Controlling Pests, Plant Diseases, and Weeds Allowed to be Used in Agriculture". It contains the names of the pesticides that may be used in the current year, their rates of use, restrictions in their application for individual crops, in the use of treated areas and of the products obtained from them.

Every year, new, effective, and, as a rule, less toxic substances tested in field conditions are included in the list. The use of pesticides that are more toxic, capable of accumulating, or characterized by unfavourable remote consequences is prohibited or restricted. Consequently, when employing pesticides, it is necessary to adhere to the list of them approved for the current year, and also to the instructions on the application of the pesticides compiled in strict conformity with the requirements adopted for the relevant substances. Orientation on old lists or publications several years old may lead to a major violation of the existing restrictions in the use of pesticides.

The recommended rates of use of pesticides must be observed especially strictly. Excessive use of a pesticide may lead to a too large accumulation of it in the environment and in the products obtained.

To protect the health of the population and prevent the circulation of pesticides in nature, sanitary norms have been established for the **maximum tolerated concentrations** of pesticides in the air of the working zone, in the atmospheric air, in the water of open basins, and in the soil (Table 3). Of special significance is control of the amount of pesticides in the soil because the latter may be, as it were, a storehouse of pesticides and the source of contamination of food products, water basins, and the air. Here account must be taken of the persistence of pesticides in the soil, their ability to migrate, their influence on the biology of the soil, their ability to be absorbed by plants and have a phytotoxic action, change the organoleptic properties of food products and potable water, of their toxicity to warm-blooded animals, and their ability to accumulate.

Table 3. Maximum Tolerated Concentration of Pesticides in Water, in the Air of the Working Zone, and in the Soil

Pesticide	Soil, mg/m³	Air, mg/m³	Water, mg/litre
HCH (mixture of isomers)	1.0	0.1	0.02
Lindane (gamma-HCH)	1.0	0.05	0.02
Polychloropinene	0.5	0.2	0.004
Toxaphene	0.5	0.5	0.004
Carbaryl	0.05	1.0	0.1

The content of pesticides in the soil is controlled in the spring before field work is begun.

When the topsoil contains persistent pesticides (carbaryl, HCH, polychloropinene, toxaphene) in amounts exceeding the maximum

tolerated ones, only grain and technical crops may be grown, and surface treatment with these pesticides is prohibited.

For the sanitary control of pesticide residues in products, standard values of the tolerance levels in various food products and fodder are determined for each substance.

These indices are coordinated by the United Nations Food and Agricultural Organization (FAO) and the World Health Organization (WHO).

The values of the maximum tolerated residual amounts (tolerance levels) are established from the results of tests involving the studying of the toxicity of a pesticide to animals and from the determination of the dynamics of the residues in the relevant culture. Cultures differ substantially in their ability to accumulate pesticides (Table 4). For example, with a toxaphene content in the soil of 10 mg/kg, plants absorbed from 2 to 46 mg of the pesticide per kg of their mass.

Table 4. Content of Toxaphene Residues in Various Agricultural Crops (after P. Lyubenko and K. Stefansky)

Crop	Content of toxaphene, mg/kg		
	surface part of plants	root vegetables	
		skin	pulp
Annual grasses	46.10	—	—
Alfalfa	2.00	—	—
Corn	2.64	0.63 (grain)	
Carrots	5.24	26.00	1.51
Beets	2.40	6.83	1.20
Potatoes	2.54	3.54	0

The **tolerance level** of a toxicant is expressed in milligrams of the active ingredient of the pesticide per kg of the product and is established to ensure for humans a safe level of the residual pesticide content in their food ration.

The tolerance level is established for each pesticide and each kind of agricultural product. It varies in different countries (Table 5).

The smallest values of the tolerance levels are established for dietetic food products (milk, eggs, meat), and somewhat higher ones, for vegetables and fruit.

For example, in the USSR, the tolerance level of HCH (a mixture of hexachlorocyclohexane isomers) in meat, eggs, milk, dairy products, and sugar must never exceed 0.005 mg/kg, in cereal crops—0.2 mg/kg, in potatoes and vegetables—0.5 mg/kg.

No residues of heptachlor, carbaryl, 2,4-D, mercury compounds, polychloropinene, parathion-methyl, thiram, etc. are tolerated in any food products in the Soviet Union.

Table 5. Tolerance Levels of Pesticides in Food Products, mg/kg

Pesticide	Recommended by FAO/WHO	Adopted in the USSR	Adopted in the USA
Lindane	Meat, eggs 0 Cereals 0.5 Vegetables, fruit 3.0	Meat, eggs, milk 0.005 Potatoes 0.5	Meat (in fat) 7 Vegetables, fruit 10
DDT	Milk 1.25 Vegetables, fruit, meat 3.5-7.0	Vegetables, fruit 0.1 Milk, meat, eggs 0.005	Milk 1.2 Vegetables, fruit, meat 3.5-7.0
Carbaryl	Meat 1 Vegetables, fruit 10	Fruit, berries, corn 0	Eggs, milk 0 Meat, poultry, 0.5 Vegetables, fruit 10.0
Dimethoate	Tomatoes, pepper 1.0 Vegetables, fruit 2.0	Fruit 1.0	Milk 0.002 Meat 0.02 Vegetables 2.0
Methyl bromide	Flour 50	Grain 35	Grain 50.0

The magnitudes of the tolerance levels vary with progress in investigations of the toxicity of pesticides and their influence on the environment.

The tolerance levels are used to establish the **harvest time**—the time that must elapse after the last treatment with a pesticide before a crop may be harvested. All pesticides applied to plants or incorporated into the soil not later than the harvest time remain in amounts not exceeding the tolerance levels or completely decompose.

The harvest time is determined by the persistence of the substance, the duration of its remaining in the environment and products, and also by its toxicological and sanitary properties and depends on the physicochemical characteristics of the active ingredients, the formulation, the object being treated, and the soil and climatic conditions. For rapidly detoxicating slightly toxic substances, the harvest time is 2 to 20 days, and for more toxic ones, 1 to 2 months.

The harvest time for most organophosphorus compounds is 15-30 days; in conditions of greenhouses and hotbeds, compounds such as malathion may be used two or three days before gathering the vegetables provided that they are thoroughly washed with water.

It is permitted to use HCH in small amounts (up to 1 kg/ha) for treating cabbage in the seedling stage, sugar beets not later than 75 days before harvesting the crop, and cotton not later than 30 days

before harvesting. When HCH is incorporated into the soil to kill soil-dwelling pests, the growing of potatoes, carrots, table beets, and other root vegetables intended for food is permitted not earlier than in four years after the treatment.

When persistent pesticides nevertheless have to be used within shorter periods or on crops in which they may accumulate, *regulations for using the products obtained are established.* For example, it is forbidden to use the tops of sugar beets and potatoes as cattle fodder and silage if less than 75 days elapsed after treatment with HCH. When orchards are treated with HCH, it is prohibited to use the grass from the inter-row spacings as cattle fodder.

To prevent the possible poisoning of workers on fields treated with pesticides, the periods when work is permitted on such fields (the reentry times) and the conditions of work on them are regulated.

For example, after the use of persistent pesticides such as HCH, work not associated with soil cultivation may be performed after six days on such fields, while work associated with cultivation of the soil may be performed after two weeks.

When pesticides are used with a high dermal toxicity (dimethoate, metasystox), work on the treated fields not associated with the workers contacting the plants contaminated with pesticides is permitted after three days have elapsed, and work associated with their contacting the plants—after two weeks. In dry hot weather on areas with dense and poorly ventilated vegetation, the reentry time is two weeks after treatment.

An important condition for ensuring the safety of workers and protection of the environment from contamination with pesticides is the strict observance of the safety rules in the storage, transportation, and use of toxicants in agriculture released by the USSR Ministry of Agriculture and approved by the USSR Ministry of Health.

The regulations, instructions, and orders issued by the USSR Ministry of Agriculture on the protection of plants are obligatory for collective and state farms and for other enterprises and organizations regardless of their departmental subordination, and also for all citizens.

Strict observance of the standards and rules adopted in the USSR for controlling the use of pesticides will ensure reliable prophylaxis of poisoning and effective protection of the environment.

4.3. Measures of Personal and Public Safety When Working with Pesticides

When working with poisonous chemicals, one must observe the instructions on safety in the storage, transportation, and use of pesticides, and also the methodological instructions on the use of individual toxicants.

All work involving the chemical protection of plants is performed under the guidance of a specialist in plant protection. The direct organizers of the work involved in the chemical protection of plants (technicians, brigade and team leaders) are chosen from among persons having the relevant experience of work and a special education, or who have received training at courses on the subject.

The heads of farms are responsible for labour protection and safety.

Persons at least 18 years old who have passed a medical examination and have been instructed on the safety rules when working with toxicants are allowed to work with pesticides.

Juveniles, nursing and pregnant women are not permitted to work with pesticides. In addition, men over 55 and women over 50 are not permitted to prepare working mixtures, treat seeds, or fumigate plants.

Persons constantly working with pesticides must periodically pass medical examinations—once a year. When working with virulent and highly toxic chemicals, the duration of the workday is four hours, and when working with chemicals of other groups—six hours. The remaining worktime is used for work not associated with pesticides. On the days of work with pesticides, the workers are supplied with milk. The organization responsible for performing the work issues protective outer garments and individual means of protection to all workers handling toxicants. Medicine kits are provided at the workplaces.

Especially responsible and dangerous work (the gassing of large premises, treatment with virulent and highly toxic substances) is performed with the participation of a medical worker on duty.

4.4. Safety Measures in Storing, Dispensing, and Transportation of Pesticides

Toxicants may be delivered from the main stores only when the given enterprise has workers prepared for working with toxicants, means for individual protection, a store meeting the requirements of the sanitary inspectors, which is controlled by the sanitary epidemic stations and confirmed (by a certificate) by the district agricultural department.

The premises for storing toxicants, and also the areas for filling the apparatus with them and preparing poisoned baits must be not closer than 200 m from dwellings and livestock buildings, sources of water supply, places of concentration of beneficial animals and poultry, and not closer than 2000 m from the shores of basins used for fish farming. The territory of a store with an area adequate for the driving in and turning of vehicles, a canopy under which containers are stored, and with an area for neutralizing the containers is reliably fenced in.

The store premises must be big enough with a view to the volume of the toxicants to be stored. The roofs must be in good order, and the floors paved with asphalt or cement. The premises must be provided with racks, natural (windows), or forced ventilation. The premises must consist of two parts: one for storing and issuing the chemicals, and the other, an auxiliary room, for storing the documents, protective outer garments, medicine kits, soap, and water. The floors in the premises must be smooth and above the level of the soil. Special attention must be given to ventilation of the store premises.

Food products, fodder, and various implements must never be kept in a toxicant store. The store must be reliably locked, and virulent poisons must be stored in a special compartment that can be sealed.

Volatile hygroscopic pesticides are stored in sealed containers. Pesticides containing water, formalin, metam-sodium, the amine salt of 2,4-D, and all oil emulsifiable concentrates must be stored in heated premises in cold weather. Magnesium chlorate and calcium chlorate chloride must be completely isolated from other pesticides because these substances cause the spontaneous ignition of combustible toxicants.

The storekeeper is responsible for the storage and issuing of the toxicants. He receives and issues them, sees to their certification, the intactness of the containers, neutralizes the containers, and cleans up the premises. It is prohibited to deliver uncertified toxicants to the stores of collective and state farms.

The containers must be marked with warning stripes: white for defoliants, black for insectoacaricides and nematicides, green for fungicides, blue for disinfectants, yellow for zoocides, and red for herbicides.

The presence of outsiders in the store is prohibited. The work involved in issuing and receiving toxicants is performed with the use of protective means. It is prohibited to take food, smoke, or work without protective outer garments at a store.

A record of received and issued pesticides is entered in an account book kept by the storekeeper in a locked desk.

A toxicant is issued from the store, according to a written order of the head of the farm or his or her deputy, to the person responsible for performing the work with the toxicants. The latter are issued only by weight in a reliable container. It is strictly prohibited to issue toxicants to unauthorized persons.

When there are perishable pesticides at a store, they must be analysed before use for determining the content of the active ingredient and correcting the rates of use. This relates first of all to the following substances:

(a) pastes, emulsifiable concentrates containing water, and colloidal sulphur subjected to drying;

(b) metam-sodium and the amine salt of 2,4-D, that may crystallize;

(c) ethylmercury chloride, calcium cyanamide, and lime because of volatility or a chemical change;

(d) formalin owing to its ability to polymerize and the precipitation of paraform.

At the end of every year, an inventory is made at a store; a report on the remaining toxicants is drawn up and signed by the chairperson of the inventory committee, agronomist, accountant, and storekeeper.

The residues of pesticides prohibited for use in agriculture or that have become unfit for use are destroyed in accordance with special instructions.

Toxicants are transported in the presence of the responsible person. It is prohibited to transport pesticides in bulk or in faulty containers. The vehicles used to carry pesticides must be in good order, and be easy to clean. It is strictly prohibited to carry pesticides together with food products or other commodities. After transportation, the vehicles are neutralized.

Usually a day's norm of pesticides is conveyed from the store to the workplace. The residues of unused pesticides together with the containers are returned to the store with the drawing up of a special report to this effect.

4.5. Safety Measures When Using Pesticides

Safety measures when using pesticides are aimed at preventing the poisoning of the workers by the toxicants, contamination of the environment, and the contact of outsiders and animals with the pesticides.

In all cases when pesticides are to be used, the supervisor of the work must notify the management of the farm in which the work is to be done, the heads of neighbouring farms, and the local population at least two days in advance on the time and nature of the work to be done and the safety measures.

Standard warning signs are set up at a distance of at least 300 m from the boundaries of the section to be treated. Workers may enter sections treated with pesticides for performing field operations in 4-6 days after the use of polychloropinene and toxaphene, in 3 weeks after the use of hexachlorobutadiene, and in 3-5 days after the use of other pesticides.

Special attention must be given to the strict observance of the safety rules when working with virulent, highly toxic, and volatile pesticides.

Preparation of Poisoned Baits. When controlling rodents, virulent poisons and highly toxic substances are used to prepare poi-

soned baits. The latter are prepared either in a specially assigned room provided with an exhaust hood or on special areas at a distance of at least 200 m from dwellings and livestock buildings. The poisonous substances obtained for the preparation of baits are guarded. Their residues are returned to the store or kept in a specially assigned room. The preparation of baits is mechanized. This not only speeds up the work, but also ensures its safety. The workers must use means for protecting their skin, eyes, and respiratory organs.

Baits must be used on the day of their preparation. Unused baits are handed in to the toxicant store for storage or are handed over to another farm where rodents are being controlled against a receipt. Small residues of baits unsuitable for use are placed into a pit, fuel is poured over them, and they are burned. The implements, containers and auxiliary materials used for preparing baits are washed with soapy hot water after work.

Implements not lending themselves to cleaning and containers are destroyed or neutralized if they are to be used again. Wooden objects are burned, metal ones are crushed and buried.

The area where the baits were prepared is ploughed to a depth of at least 25 cm with turning over of the soil layer and is covered with slaked lime. Only after this has been done is the guard lifted.

To avoid poisoning, the open placing and scattering of poisoned baits are prohibited in populated localities and around them within the boundaries of the grazing land for cattle and poultry, around farms within a radius of 500 m, at place of concentration of beneficial wild animals and birds, and also on the adjoining land within a radius of 200 m.

In these cases, the baits are placed into the burrows or other shelters. The aerial scattering of poisoned baits containing zinc phosphide is performed only with special permission of the USSR Ministry of Agriculture as an exception.

It is forbidden to graze cattle on the territory treated with baits during the period indicated in the relevant instructions.

Fumigation of Premises and the Soil. All fumigation jobs, owing to their special hazard, are performed by skilled specialists, and only with permission of a sanitary inspector. All objects being gassed are to be guarded around the clock up to completion of the work.

Gassing may be performed only in premises meeting the requirements of hermetic sealing and arranged not closer than 200 m from dwellings and 100 m from farm buildings. Fumigation is performed at a temperature of the air outside and inside the premises not under 10 and not over 35 °C.

To ensure safety, the work is done by a brigade divided into teams of three. They all work in overalls, gloves, special shoes, and gas masks with a filter of the corresponding grade.

A restricted zone is marked out around the object, and warning signs "No entrance! Gas!" are put up.

All the work involving the admission of a gas into premises is performed with account taken of the properties of the gas and its container. When working with flammable fumigants, the objects being treated are disconnected from the electric mains, and special fire safety measures are taken.

After gassing, the objects are degassed, the gas being removed from the premises and the materials in them by natural or forced ventilation with the observance of the safety rules. The time needed for degassing is determined by the object, the properties of the fumigant, and the method of degassing. Large objects should be degassed gradually to prevent large amounts of gases escaping into the atmosphere. The supervisor of the work issues written permission for use of the object.

Seed Treatment. Highly toxic substances are often used to treat seeds. Consequently, this work may be done only when using apparatus in good order and serially manufactured machines (PSSh-3, PS-10, etc.) outfitted with a cleaning device. Reliable means for protecting the body, eyes, and especially the respiratory organs are obligatory.

The treatment of seeds with the use of adhesives reduces the concentration of pesticide vapour in the working zone to one-ninth of its value without them.

It is prohibited to treat seeds in barrels and by scooping. Treatment is performed on an open site or under a canopy at a distance of at least 200 m from dwellings.

Treatment may be carried out indoors only with good ventilation.

The chemicals and the treated grain are strictly accounted and stored in special premises.

It is prohibited to use treated grain for food purposes, and also for feeding to animals or poultry, to mix it with untreated grain, and to sell it in any way.

Ventilation, washing, cleaning, and baking do not free the products of toxicant residues.

Treated grain is stored separately from food products and fodder and is reliably guarded. Treated grain is issued for sowing only when ordered by the head of the farm or his or her deputy. The issuing is covered by a document—an invoice.

Treated seeds are to be transported to the place of sowing in sacks of a dense fabric, and only in exceptional cases, upon special permission of a sanitary inspector, is transportation in canvas-covered motor vehicles permitted. It is strictly prohibited to convey people on vehicles together with treated seeds, even if the latter are covered with canvas.

In sowing, the workers attending to the sowing machines are provided with a set of individual means of protection. When sowing, the lid of the seedbox must be tightly closed, and the seeds in the machine must be levelled out with a shovel (by no means with the hands!).

Residues of treated grain are returned to the store, while small amounts of spilled out grain are burned and the ashes buried. The place where the treated grain was kept and its containers are neutralized. Vehicles after the transportation of treated grain and sowing machines after sowing are thoroughly cleaned and neutralized.

Spraying and Dusting Pesticides and Use of Aerosols. All this work is performed only using mechanisms. Spraying and dusting should be performed in the morning and evening, and in dull weather in the daytime too. Treatment must never be performed before or during a rainfall.

The rates of use of the pesticides and the treatment periods must be strictly controlled.

Specially equipped filling areas must be provided for preparing the working formulations of the toxicants.

Preparation of the working liquids and filling of the reservoirs of the spraying machines with virulent and highly toxic pesticides must be completely mechanized. It is prohibited to prepare dusts directly at farms. Special machines (MAG-1, AG-UD-2), the device AP to the OTN-8-16 machine, and aviation equipment are used to prepare aerosols, or insecticide smoke pots "Gamma", G-17 and the like are used. Aerosols are used in the open air with a slight wind (up to 2 m/s) or in hermetically closed premises. After treating closed premises with aerosols, they must be ventilated for 24 hours.

The working solutions are poured into the tanks of the machines through filters to prevent clogging.

Persons occupied in preparation of the working solutions and participating directly in the spraying and dusting with pesticides must be provided with individual means of protection. When working, one must see that the spray is directed by the air current away from oneself.

Upon the completion of work, all the apparatus must be cleaned, washed with a soda solution and water, dried, and handed in to the store.

Grazing of cattle on treated areas and on areas within a radius of 300 m from the boundaries of the plots treated with toxicants is permitted not earlier than in 25 days after treatment (for especially toxic and persistent pesticides this period is longer and is indicated in special instructions). It is prohibited to feed weeds from fields treated with pesticides to livestock.

4.6. Neutralization of Vehicles, Containers, Premises, and Protective Garments

Neutralization is conducted with substances detoxicating the pesticides. Vehicles, containers and garments are neutralized in the open air on a special site with a paved surface and a sewer for water. The neutralizing means after their use and the washing water are drained off into special cesspits at least one metre deep. The pits are dug at places where the groundwater table is at least two metres from the surface, subject to approval by the local health authorities. As the cesspit is filled, each layer is treated with a paste of slaked lime. As soon as the pit is filled up to 0.5 m from the surface, it is covered with soil.

Vehicles and apparatus used for work with pesticides must be neutralized at least twice a month with a bleaching lime paste (1 kg of lime per 4 litres of water), which is washed off with water in one hour after its application.

Metal and glass containers (barrels, cans, drums, jars) contaminated with organophosphorus, organochlorine compounds, and derivatives of dinitrophenol and other pesticides are neutralized with alkaline solutions (soda, wood ash, lime). The containers are filled with a 5% solution of caustic or washing soda and left standing for 6-12 hours, and are then repeatedly washed with water. When wood ash is used, the containers are filled with it, water is added to form a paste, the contents are mixed and left standing for 12-24 hours, after which the contents are poured into a cesspit. The external parts are washed with brushes, or rags wetted in the same solution. Sacks are wetted for 4-5 hours in a 2% solution of soda ash and are then boiled in a soap and soda solution for 30 minutes.

Containers emptied of mercury-containing pesticides are neutralized with one of the following means: a 30% solution of iron(III) chloride; a 0.2% solution of potassium permanganate acidified with hydrochloric acid (5 ml/litre); the paste "Pereguda" (a mixture of pyrolusite and 5% hydrochloric acid in the proportion 1 : 2); a paste of lime chloride (1 kg per 4 litres of water). A container is filled with one of the solutions and left standing for 5-6 hours. It is next treated with a 1% solution of potassium permanganate and in 24 hours is washed with warm soapy water (a 4% solution of soap in a 5% soda solution).

Sacks that had been used for grain treated with mercury-containing pesticides are wetted in a 1% solution of potassium permanganate, and are then washed in a soap and soda solution.

Containers emptied of carbamine pesticides (thiram, carbaryl) are neutralized using a 1% solution of potassium permanganate acidified with hydrochloric acid (5 ml/litre) or a paste of lime chloride.

Containers emptied of dichloroethane, methyl bromide, or methallyl chloride are neutralized by thorough ventilation to remove the residues of these pesticides, and then by treatment with steam (120-130 °C) until the odour of the pesticide vanishes.

The neutralized containers are handed in to the basic stores.

It is strictly prohibited to use containers emptied of pesticides for storing food products, potable water, and fodder.

Premises contaminated with pesticides are cleaned and the floors in them washed with a solution of soda ash (200 g of ash per pail of water), and then with a 10% solution of lime chloride. Sections of soil contaminated with pesticides are neutralized with lime chloride and dug over.

Special outer garments contaminated with toxicants lose their protective properties and may be a source of poisoning, therefore they must also be neutralized. Washing of these garments must be centralized in special laundries. The garments must be delivered to a laundry in closed boxes. It is prohibited to wash protective outer garments near wells, rivers, lakes and other sources of water. The garments are neutralized by soaking them in detoxifying solutions and then washing in hot water. Garments contaminated with organochlorine pesticides are soaked in a hot 0.5% soda solution for six hours; the solution must be stirred and changed three times. They are next washed in a soap and soda solution. Garments contaminated with mercury-containing preparations are soaked in a hot 1% solution of soda for 12 hours, and then washed three times for 30 minutes each time in a soap and soda solution with the addition of alkyl sulphonate.

Protective garments contaminated with organophosphorus and other pesticides are neutralized in a soap and soda solution for 6-8 hours, after which they are washed two or three times in a hot soap and soda solution.

Rubber shoes, gloves, and aprons must be treated with a lime chloride paste or a 3-5% solution of soda ash and washed with water.

4.7. Disposal of Unwanted Containers and Pesticides

Containers emptied of toxicants are neutralized, and those suitable for further use are returned to the plant or used to store the same toxicants.

Emptied paper and wooden containers that can no longer be used are burned, and their ashes must be buried in the earth on a section at a distance from water basins and dwellings of at least 200 m. Unfit metal containers are crushed, while glass ones are broken and everything buried in a pit.

Pesticides spoiled as a result of prolonged storage or of damaging of the container, and also residues of small amounts of pesticides whose storage is not expedient, as well as working formulations that were not used in good time are to be destroyed. A report is drawn up indicating the amounts of pesticides and reasons for destroying them, and an entry is made to this effect in the register at the store.

It is permitted to destroy only small amounts (up to 10 kg) of pesticides at collective, state, and other farms. Substances containing mercury are not to be destroyed, but must be handed in.

The ways of destroying pesticides depend on the chemical properties of the active ingredient of the pesticide, the amount of the substance to be destroyed, and the conditions of destruction. A pesticide must always be detoxified before being buried in the soil.

Organophosphorus, organochlorine, dinitrophenol compounds and others decomposing in an alkaline medium are neutralized with a 5% solution of a caustic alkali or suspensions of slaked lime or lime chloride. The detoxifying compositions are poured over the toxicants to a level 15 cm higher than that of the toxicants.

After detoxification, the poisonous chemicals are buried in a pit one metre deep at a distance of at least 0.5 km from residential buildings, sources of water, or pastures.

Toxicants are destroyed under the supervision of an agronomist according to written instructions of the farm head. The place and way of destroying toxicants must be approved by bodies of the sanitary and epidemic service.

4.8. Measures for Public Safety and Protection of Environment from Pesticide Pollution

Measures for public safety are aimed at preventing the contamination of the atmosphere, soil, water sources, and food products by toxicants. The strict observance of the rules for working with pesticides excludes the accidental contact with poisonous chemicals of outsiders, ensures the protection of bees, birds, beneficial animals and insects from the action of pesticides.

To avoid creating a menace of contamination of the environment and accumulation of pesticide residues, preference must always be given to pesticides that are less persistent, less volatile, and have a lower toxicity when selecting pesticides recommended for widespread use in agriculture. If there are no sufficiently effective substitutes of stable and volatile substances, the use of the latter and the conditions of working with them are strictly regulated.

The atmospheric air and water basins may become contaminated as a result of the drifting of pesticide particles in dusting, spraying, and using aerosols, as a result of violation of the rules for fumigation, and of the storage and transportation of pesticides in dam-

aged containers, upon treatments in windy weather, and when soil particles are carried off treated fields.

To avoid the drifting of toxicant particles, aerial dusting, fine-drop spraying, and aerosol treatments are prohibited within a radius of 1000 m around populated localities, farmsteads, and within a radius of 2000 m from the shores of fish-farming basins. The use of pesticides must never be attended by their entry into the atmospheric air of populated localities in concentrations exceeding the maximum tolerated ones.

It is prohibited to perform spraying, dusting, seed treatment, or bait preparation outdoors if the wind speed exceeds 3 m/s. Aerial dusting is prohibited if the speed of the wind exceeds 2 m/s, fine-drop spraying if it exceeds 3 m/s, and large-drop spraying if it exceeds 4 m/s. To reduce the drift of pesticides in aerial treatment, new formulations of pesticides such as inverted emulsions are being developed.

The aerial treatment with chemicals of areas closer than 1 km to populated localities is prohibited.

Aerosols may be used only in calm weather or with a slight wind (up to 2 m/s). Fumigation is not permitted if the wind's speed exceeds 7 m/s.

Soil, owing to its high biological activity and certain agrochemical properties (acidity, absorptivity, etc.) is characterized by an inactivating ability. But upon the frequent use and large rates of consumption of persistent toxicants, they may accumulate in the soil in considerable amounts. A limited use of persistent pesticides, a strict observance of the rates of use, and the alternation of pesticides of different groups prevent the accumulation of their residues in the soil. Normalization of the maximum permissible residues of pesticides in the soil makes it possible to control and regulate the circulation of pesticides in nature.

It is strictly prohibited to bury and plough into the soil large amounts of pesticides with the aim of destroying them.

Near livestock barns and water basins, it is prohibited to erect premises for the storage of pesticides and for working with them, to provide filling sites, pits for sewage after neutralization and for destroying pesticide residues.

Parks and green plantings within the confines of populated localities are treated only with pesticides of a moderate and low toxicity having no unpleasant odour, using surface vehicles and machines. This work must be done at night or early in the morning.

It is not good to treat areas over five hectares at a time. No pesticides may be used for treatment on the territory of hospitals, schools, kindergartens, or sports grounds.

The entire local population is to be informed about the places, times, and nature of chemical treatments in good time before com-

mencing them. This is done to allow the inhabitants to take the relevant safety measures (stop the grazing of cattle, the flight of bees, and field work, cover wells, etc.).

Warning signs are set up on the treated areas and on the zone around them at least 300 m wide. On fields, hay lands, and pastures treated with persistent pesticides, it is prohibited to graze cattle during the time indicated in the instructions for the use of the relevant substance.

It is prohibited to feed fodder contaminated with pesticides to agricultural animals.

There must be no people, animals, or birds when an area is being treated with an aerosol. Forest areas may be treated only if they contain no pastures. It is prohibited to scatter baits or lay them out in the open at places of accumulation of beneficial wild animals and birds, and also on the adjacent land within a radius of 200 m.

To protect bees from the action of toxicants dusted or sprayed within a zone of at least 5 km from the bee gardens, it is necessary either to move the hives to another place of honey gathering, or remove the hives into winter huts, or isolate them in some other way for a period up to five days depending on the kind of pesticide. When a real danger appears to the bees, it is necessary to use pesticides less dangerous to them, perform chemical treatment in the late evening when the bees do not visit plants, give preference to spraying instead of dusting, and use surface treatment instead of aerial spraying.

Crops should be treated with poisonous chemicals only if there is a real danger of yield depression. It is strictly prohibited to treat fields not requiring chemical means of protection even if the treatment was planned beforehand.

To control the application of chemicals at farms, special books must be kept in which for each field the time of treatment is entered, as well as the rates of use of the pesticides and the conditions of performing the treatments. The entries are made and signed by the person responsible for the work, the chief agronomist of the farm, and also the brigade or team leader, and are an official document in checking the quality of the work, in sanitary control of the products, and for filling in the relevant certificate when products are being shipped for sale or are purchased by the state. The recommended rates of use must be strictly observed in treatments, and the use of excessive amounts must never be tolerated. Special attention must be given to strict observance of the harvest time. No pesticides are permitted to be used on strawberry and raspberry plants after they have blossomed. It is not allowed to use chemicals for surface treatment to protect cultures employed in the food in the form of greens (scallions, dill, lettuce, parsley, leaf beets, carrots). In this case, what is permitted is only treatment of the seeds and soil before the seedlings appear

provided that the products do not acquire toxic or foreign organoleptic properties.

The state sanitary inspection bodies must conduct planned control of the content of residual amounts of pesticides in food products. Products containing the residues of pesticides relating to virulent and highly toxic substances in amounts exceeding the tolerance level may not be used as food except for those subjected to heat treatment that causes the pesticides to decompose.

Products gathered from test plots when testing new pesticides not yet approved for widespread use are not to be sold until special permission is given to this effect by bodies of the Ministry of Health.

The heads of enterprises using pesticides bear full responsibility for the harmlessness of the food products and fodder they produce.

4.9. Means for Individual Protection of Workers Using Pesticides

To prevent pesticides from getting into their organisms through the skin, respiratory organs, and mucous membranes, all workers must be provided with means for individual protection.

In selecting the means for individual protection, account is taken of the physicochemical properties of the pesticides, their toxicity, the way of application, and the conditions of work.

Each worker is given individual means of protection of his size that are stored in a special clean and dry room in separate lockers.

Special clothing, gloves, and boots are used to protect the skin. When working with dusty substances, one must use overalls of a dustproof fabric with a smooth surface such as moleskin. When spraying or working with liquid pesticides, one must use clothing made from acid-proof fabrics or dustproof overalls with a film-coated apron and arm sleeves made from a rubberized fabric or Textovinit.

Canvas footgear is used for protection when working with dusty toxicants, and rubber boots when spraying. Rubber gloves (article 374) are used to protect the hands when working with liquid forms of pesticides, and cotton gloves with a film coating and acidproof impregnation (KR) or combined gloves with Textin palm guards when working with dusty toxicants.

It is prohibited to use medical rubber gloves to protect the hands in performing any kind of work.

To protect the eyes from pesticides, one must use hermetic goggles PO-2, "Monoblok" goggles, or protective enclosed goggles SZZM-bts.

Antidust or antigas (universal) respirators and gas masks are used to protect the respiratory organs. It is strictly prohibited to use gauze bandages.

When working with dusty substances whose volatility at ordinary temperatures is not high (copper oxychloride, simazine, thiram, etc.), antidust respirators may be used. When dusting or spraying plants and when treating seeds with highly toxic volatile compounds, gas mask respirators with gas mask filters of the corresponding grade must be used. When fumigating premises with highly poisonous substances such as methyl bromide, industrial gas masks with cases "A" coloured brown must be used.

Antidust Respirators. The simplest means for protecting the respiratory organs is a type "Lepestok" respirator. It consists of two round pieces of gauze between which a layer of a special fabric is sandwiched that has a high dust-trapping ability. The respirator is conveniently secured on the head with the aid of laces and flexible plates and tightly fits against the face. The exhaled vapour moistens the fabric, as a result of which it gradually loses its protective properties, therefore such a respirator may be used only during one shift (a one-time respirator). This respirator cannot be used in a rainfall, fog, or stored in damp premises. It provides good protection from dust particles of substances with a low and moderate toxicity only in conditions of a normal humidity.

The "Lepestok" respirators are manufactured in three types: "Lepestok-200" protects from highly dispersed dust contained in concentrations up to 200 MTC (maximum tolerated concentration), "Lepestok-40"— from fine and medium dispersed dust in concentrations up to 40 MTC, and "Lepestok-5"—from fine and medium dispersed dust in concentrations up to 5 MTC and from coarse dispersed dust in concentrations up to 200 MTC.

The antidust respirator U-2K consists of a filtering half-mask whose outer layer is made from a large-pore polyurethane cellular plastic, and whose inner layer is made from a thin polyethylene film in which an inhalation valve is installed. The space between the two layers is filled with a filtering material made from synthetic fibres. The front part of the half-mask accommodates the exhalation valve also used to remove the moisture accumulating inside the half-mask during respiration. The air is cleaned by filtration through the entire surface of the half-mask. The respirator protects the respiratory organs from highly dispersed dust of pesticides having a low or moderate toxicity. The average period of use is 30 days.

The antidust respirator F-62Sh has a filtering box with replaceable filters, and a rubber half-mask with an exhale valve installed in it. This respirator protects the respiratory organs from pesticides having a low or moderate toxicity that are suspended in the air in the form of a highly dispersed dust. The average service life of a respirator is one year, and of a filter, 30 days. Antidust respirators do not protect the respiratory organs from the gases and vapours of poisonous substances.

Antigas Respirators. The antigas respirator RPG-67 consists of a rubber half-mask in which there are installed an exhalation valve and two antigas filtering cartridges. The absorber filling a cartridge determines the type of cartridge (A, V, G, KD) in a respirator and its designation: RPG-67-A protects from phosphorus- and chlorine-containing organic pesticides, RPG-67-V from acid gases (sulphur dioxide, hydrogen sulphide, hydrogen chloride), and also from phosphorus- and chlorine-containing pesticides, but with a smaller duration of protection than with an A-type cartridge, RPG-67-G protects from mercury vapour, and RPG-67-KD from hydrogen sulphide and ammonia.

The universal respirator RU-60M is similar in its design to the RPG-67 model, but its cartridges contain, in addition to absorbents, aerosol filters ensuring the simultaneous protection of the respiratory organs from harmful substances in the air in the form of vapours, smoke, gases, dust, and mist. The types of the respirator and their application are determined by the cartridge types.

Antigas respirators may be used when the concentration of poisonous substances in the air does not exceed 10 MTC. When working with virulent and very volatile substances, and also when the concentrations of the poisonous vapours and gases exceed 10 MTC, it is prohibited to use respirators. In these cases, gas masks must be used to protect the respiratory organs.

The duration of protective action of antigas respirator cartridges is determined approximately according to tables compiled for each type and depends on the concentration of the toxicants in the air of the working zone. When working with mercury seed disinfectants, a type G cartridge should be used for protection not over 70 hours, and a type A cartridge, not over 50 hours, provided that the treatment is being performed in the open air.

The persons responsible for performing the work must fill in a certificate for each antigas filter box in which the duration and conditions of its service are indicated.

Spent cartridges to respirators and filter boxes of gas masks must be replaced in good time.

Respirators are selected by their size and are allotted to definite persons. They ensure reliable protection when properly used, when stored in a dry and clean room, and when regular prophylactic care is taken of them.

Every day after work, contaminated rubber face parts and corrugated tubes are washed in a neutralizing solution (25 g of soap and 5 g of soda per litre of water) or in a solution of DIAS (100 g of DIAS per 10 litres of water), with obligatory washing in water and drying in the air. After this, the face parts and tubes are disinfected with alcohol or a 0.5% solution of potassium permanganate.

4.10. Personal Hygiene Rules for Workers Using Pesticides

Work with chemical means of protecting plants must be performed with great care, special attention, and precision. Persons using toxicants must be able to select and properly use the means for individual protection.

The prevention of poisoning by pesticides is determined to a major extent by the strict observance of the instructions and of the personal hygiene rules.

The toxic action of pesticides on a human depends on the state of his or her organism, therefore rational conditions of work, nutrition, and recreation must be observed in the period of working with them. Smoking is prohibited when using toxicants because this facilitates the entry of the poisonous substances into the organism. The action of toxicants on persons drinking alcoholic beverages before or during work is amplified scores of times, and this is why the use of such beverages is strictly prohibited.

An important role in the prevention of poisoning is played by rational nutrition, which increases the resistance of an organism to the action of poisonous substances. The food must be rich in proteins, vitamins, and it should preferably contain products having enveloping properties (starch, gelatin) that diminish the irritating action of chemical compounds and prevent their being sucked in.

Food must be taken before beginning work with toxicants. The absence of food in the gastro-intestinal tract creates conditions promoting the more rapid suction of chemical substances into the blood and increasing the harm to the organism. The breakfast and lunch of persons working with pesticides must contain an adequate amount of liquid, not very salty food (soups, milk, stewed fruit, tea). Such food facilitates the rapid excretion of poisonous substances from the organism. It is not good to use food products retaining water in the organism (salty fish, vegetables, etc.).

Persons working with organochlorine pesticides must use food rich in animal proteins (meat, cottage cheese, fish), calcium salts, and vitamin B_2 (riboflavin). Fats must be avoided because they facilitate the suction of poisonous substances into the organism.

The food ration of persons handling organophosphorus compounds must include cottage cheese, cheese, sour milk, sugar, vegetables, fruit, greens, buckwheat porridge, and a large amount of vitamin C. Spicy dishes and fats must be avoided.

Persons working with copper-containing pesticides must use food products rich in proteins and vitamins (beef, porridge, vegetables, fruit, sugar, honey). Workers having to do with copper-containing pesticides must never use fats and milk in their food, and those handling zinc phosphide must not use eggs, fat, and milk.

Persons working with toxicants must wash their hands and face with soap and rinse their mouth before eating. After finishing work, they must take a shower.

Chapter 5

PHYSICOCHEMICAL FUNDAMENTALS OF PESTICIDE APPLICATION

5.1. Pesticide Formulations

The successful use of pesticides to control pests, plant diseases, and weeds depends not only on their toxicity with respect to the harmful organisms, but also to a considerable extent on the form of the pesticide. The formulation determines how a pesticide is used. The following formulations are manufactured for the protection of plants:

powders (dusts) for dusting, wettable powders forming a suspension with water;

granulated formulations both for treating plants and for incorporation into the soil;

solutions in water and organic solvents;

emulsifiable concentrates forming emulsions when diluted with water, microencapsulated formulations, and pastes.

Pesticides are also used in the form of aerosols and fumigants.

Also prepared are poisoned baits, various antiseptic and insecticide soaps, paints, and insecticide paper.

Powders (dusts) are a mechanical mixture of an insecticide, a fungicide or herbicide, and a well comminuted filler or carrier.

In dusting, from 10 to 30 kg of the dust are used per hectare, therefore its pesticide content must be adequate to ensure the proper action of the formulation. The content of the active ingredient (toxicant) in a dust must correspond to the relevant USSR State standard.

Talc, pyrophyllite, chalk, kaolin, tripoli (diatomite), silica gel and various clays are used as carriers to prepare dusts. Preference is given to talc and pyrophyllite because they have a stratified structure and therefore adhere better to plants.

In all cases, the substances used as carriers must never change the chemical properties of the pesticide (for example, alkaline and acidic carriers may cause the hydrolysis of the esters of phosphorus and other substances, carriers of hydrophilic minerals such as clay and kaolin become caked in moist conditions).

To diminish unproductive dusting and losses due to the drift of fine and very minute particles, from 3 to 5% of a mineral oil is added to dusts.

Practice and numerous studies have shown that the optimal size of dust particles is 15-25 μm for surface treatment and 25-50 μm for aerial treatment. Coarser dusts (with particles 70 μm and more in size) are retained poorly on the leaves of plants.

Wettable powders are powdered formulations of pesticides that yield stable suspensions when diluted with water. The use of pesticides in the form of suspensions has substantial advantages in comparison with dusts: the unproductive losses of the toxicants are decreased because they adhere better to plants and are retained better on them in the form of suspensions. Wettable powders must meet the following requirements:

they must be stable in storage and not cake;

when diluted in water, they must rapidly form suspensions with slow settling of the solid particles;

they must wet the leaves of plants and other treated surfaces very well and be well retained on them.

This is achieved first of all because wettable powders are highly dispersed and contain 80% of particles with a diameter of 3 μm. In addition to the active ingredient and carrier, wettable powders contain surfactants and adhesives (stickers). The carriers used include silica gel, synthetic calcium metasilicate, bentonite, and kaolin. The surfactants include alkali metal sulphonates, the alkylaryl esters of polyethylene glycol OP-7 and OP-10, and also auxiliary substances—sulphite-alcohol slops, sulphite liquor, starch, and casein.

Wettable powders usually contain 30-80% of the active ingredient, 15-60% of the carrier, 1.5-2% of sulphite-alcohol slops, and 1-2% of OP-7. For instance, simazine is prepared in the form of a 50% wettable powder.

Granulated formulations are incorporated into the soil for controlling soil-dwelling pests, for intoxicating plants through their root system, and also for controlling surface pests by aerial dispersion.

Granulated formulations are prepared by impregnating ready granules of the minerals perlite and vermiculite with a pesticide and by granulating powdered formulations.

Binders—synthetic resins or other adhesive components—are introduced into the composition of the formulation in addition to the pesticide and the carrier. Usually, bentonite and kaolin are used for quickly acting formulations with a short period of toxicity, and tripoli for formulations with more prolonged action.

The average diameter of a granule is from 0.25 to 5 mm. Small granules (from 0.25 to 1.5 mm) are distributed more uniformly over the surface of the soil and plants. Large granules (from 3 to 5 mm) are distributed less uniformly, which is of no special significance for systemic insecticides, but they act for a longer period.

Granules with a diameter of 0.25 to 0.6 mm are used for application onto plants, of 0.5 to 1.5 mm (contact, contact-fumigation) for scat-

tering over the surface of the soil, and of 2-3 mm (contact-fumigation) or 3-5 mm (systemic) for incorporation into the soil.

Granules must not contain dust because when dispersed aerially the latter will drift over large distances.

Insecticides, nematicides, and herbicides are mainly formulated as granules.

When granulated pesticides are used, their losses due to drift are diminished, the burning action on plants is smaller, entomophags are not killed, and the danger to humans and beneficial animals is lowered.

Solutions of pesticides in water and in organic solvents. Pesticides with a good solubility in water are prepared and used as aqueous solutions. They include certain herbicides (salts of MCPA, 2,4-D, and MCPB, diquat, banlen, etc.), insecticides, and fungicides.

Aqueous solutions of pesticides are not convenient for storage and transportation, require large storage capacities, evaporate, and freeze in cold weather.

Aqueous solutions wet leaves poorly because water has a large surface tension, therefore, surfactants such as OP-7 and OP-10 have to be added to them.

Solutions of pesticides in various organic solvents have come into great favour, especially for small-scale and economical spraying. Petroleum hydrocarbons, deodorized kerosene, diesel fuel, or mineral oils are used to prepare pesticide solutions.

Varnishes, lacquers, and paints to which insecticides, fungicides, or antiseptics have been added may also be related to solutions.

Emulsifiable concentrates are a solution of a pesticide in oil comminuted into fine drops coated with a protective layer of a surfactant. When diluted with water, they form stable emulsions that do not stratify for a long time. The oil droplets with the pesticide dissolved in them are the dispersed phase in such an emulsion, and water is the dispersing medium. Emulsifiable concentrates are prepared with the use of homogenizers.

Two kinds of emulsifiable concentrates are distinguished. Those of the first kind are obtained by dispersing in water a solution of a pesticide in a solvent not miscible with water. It would be more proper to call them concentrated emulsions characterized by a high degree of dispersion and stable in storage.

Emulsifiable concentrates of the second kind consist of a pesticide, a solvent, and an emulsifier. Hydrocarbons, esters, kreoline, etc. are the solvents, and calium sulphonates, OP-7, OP-10, and various soaps are the emulsifiers. To prepare an emulsifiable concentrate, the pesticide is dissolved in the solvent and mixed with the emulsifiers under heating to 40-80 °C.

For practical use, not too viscous emulsifiable concentrates are more convenient, but it is safer to use concentrates with a higher viscosity for more toxic organophosphorus pesticides because when

they get on the skin they are slowly sucked in and are washed off more readily.

Emulsifiable concentrates also include various disinfecting soaps containing antiseptics and insecticides.

Recent years have seen the introduction of what has been called **inverted emulsions,** in which the pesticide dissolved in water is the dispersed phase, and oil is the dispersing medium; the fine droplets of the aqueous pesticide solution are embedded, as it were, in the large oil drops. Inverted emulsions are used for small-scale spraying; they adhere better to plants and do not evaporate.

Microencapsulated formulations consist of capsules from 5 to 100 μm in size. The active ingredient is confined in a shell that decomposes under the action of various substances, sunlight, temperature, or mechanically. They are used when it is necessary to exclude the direct contact of humans, animals, and plants with the active ingredient for a definite time or retard its action.

The shell is made from polyamides, gelatin, agar, and other substances; the pesticide must not dissolve in the substance of the shell.

Auxiliary substances (ingredients) are intended for improving the physicochemical properties of working compositions of pesticides. Auxiliary substances improving the physical properties of working compositions of pesticides are called **bonifiers.**

When preparing dusts with a very low content of the active ingredient (1.5-2%), carriers are widely used. They must readily lend themselves to grinding, not cake in storage, disperse well when applied, and not cause decomposition of the pesticide in storage and when applied.

Talc, kaolin, and the ash from electrical precipitators are used as carriers for dusts; silica gel, bentonite, kaolin, and infusorial earth are used for wettable powders.

Talc mainly contains magnesium silicate with the general formula $H_2Mg_3(SiO_3)_4$. When talc is ground, microscopic crystalline fragments are formed. It is not hygroscopic, is poorly wetted by water, and disperses well with a low moisture content. Its density is 2.7 g/cm^3, and its free bulk mass is 0.8 kg/dm^3.

Kaolin mainly contains aqueous aluminium silicate $Al_2O_3 \times \times 2SiO_2 \cdot 2H_2O$. It consists of microscopic amorphous particles, is well wetted by water and disperses well. Its density is 2.1-2.6 g/cm^3, and its free bulk density is 0.3-0.4 kg/dm^3. Kaolin as a carrier forms lighter dusts that are less suitable for aerial application because they are carried away more by air currents; it is better to use them for dusting by surface machines.

Surfactants have a major significance for improving the physical properties of working solutions of pesticides.

They facilitate better covering and retaining of the solution on plants with poorly wettable leaf surfaces because they lower the

surface tension, the air layer between the droplets of the formulation and the surface of a leaf being eliminated. Surfactants increase the viscosity of a solution and reduce the evaporation of the drops. The result is a longer duration of contact with the surfaces of plants.

Studies have shown that these substances promote the penetration of herbicides through the cuticle and stomas into the mesophyll of the leaves and accelerate their translocation in the cells of plants.

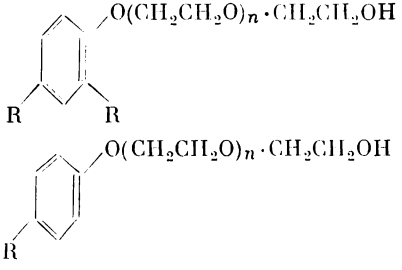
After the water evaporates from the droplets of herbicide solutions, a thin and rainproof pesticide film forms on the surface of the leaves, which facilitates longer contact of the pesticide with the plant.

These substances are stabilizers and emulsifiers in the working compositions of pesticides.

Surfactants include soap, concentrates of sulphite-alcohol slops, polyethylene glycol esters OP-7 and OP-10.

The formulations OP-7 and OP-10 in their appearance are oil-like or paste-like substances with a colour ranging from light yellow to dark brown. OP-10 is more consistent than OP-7.

In their chemical composition, OP-7 and OP-10 are mixtures of incomplete mono- and dialkylphenyl esters of polyethylene glycol:



where R is an alkyl residue containing 7-10 atoms (OP-7) or 9-10 atoms (OP-10) of carbon, and n on an average equals 6-7 (OP-7) or 10-12 (OP-10).

Both substances dissolve well in water in any proportions. Their aqueous solutions have a high surface activity, and at a concentration of 0.02-0.03% they wet leaves and the integuments of insects very well. When agitated, the aqueous solutions foam strongly and have detergent properties.

Many organic compounds that are insoluble in water dissolve well in OP-7 and OP-10, which explains their use for preparing emulsifiable concentrates of many pesticides. When such concentrates are diluted with water, stable emulsions are formed that do not stratify for a long time.

The reaction of concentrated aqueous solutions of OP-7 and OP-10 is neutral, and of dilute ones, weakly alkaline.

In the industrial manufacture of insecticides, herbicides, fungicides and the like, OP-7 or OP-10 is added to them.

The inhalation of aerosol particles of formulations of OP-7 and OP-10 may cause slight irritation of the mucous membranes in the upper respiratory tract.

Concentrates of sulphite-alcohol slops in their chemical composition are calcium salts of lignosulphonic acids with a mixture of reducing and mineral substances.

Three kinds of the concentrate are prepared for practical use: a liquid concentrate of slops—a dark brown liquid containing 50% of dry matter;

a solid concentrate of slops—a dark brown mass containing 76% of dry matter;

a powdered concentrate of slops—a light brown powder containing 87% of dry matter.

Concentrates of sulphite-alcohol slops are used as emulsifiers of emulsions and stabilizers of suspensions, and also as wetting agents and spreaders of working compositions because they have a high surface activity and lower the surface tension of aqueous solutions.

Liquid and Solid Soaps. In their chemical composition, these are potassium or sodium salts of various fatty acids.

Liquid soap in its appearance is an ointment-like mass or a thick liquid ranging in colour from light yellow to dark brown. In its chemical composition, it is a mixture of potassium salts of unsaturated acids—oleic ($C_{17}H_{33}COOH$), linolic ($C_{17}H_{31}COOH$), etc.

Liquid potassium soap is produced for practical use in which the content of fatty acids must be at least 40% and of free alkali 0.1%.

Soaps dissolve in water and yield strongly foaming solutions having a low surface tension, therefore they wet the integuments of insects and the leaves of plants very well.

Aqueous soap solutions have an alkaline reaction owing to their containing free alkalies and salts of the alkali metals. If water contains salts of calcium, magnesium, barium, copper, or iron, the soaps react with them to form insoluble salts of these metals that precipitate. This lowers the wettability of the solutions, while the salt coagulates may clog the apparatus. This is why hard water must never be used to prepare solutions of pesticides with soaps. Soaps have insecticidal properties and their use in the form of 3-4% solutions gives satisfactory results in controlling aphids and thrips. Soaps have no phytocidal action.

Solid laundry soap consists of sodium salts of high-molecular fatty, naphthenic, and resin acids. Sodium silicate and clay are added to impart hardness to the soap. The content of fatty acids, including unsaponified fat, must be at least 38-42%, of free caustic alkali reduced to NaOH—0.2, of calcined soda and silicate—not over 3 and of clay—10%. Like liquid laundry soap, solid soap precipitates from a solution in hard water.

5.2. General Characteristics of Ways of Applying Chemical Means for Plant Protection

Spraying is a widely used way of applying pesticides in the form of solutions, emulsions, or suspensions to a surface being treated.

Special equipment—sprayers (hand, tractor, and also aerial) is used for spraying.

Spraying is a universal method of applying pesticides and has substantial advantages over other methods: with a very low consumption of the active ingredient per unit of area, it is possible to ensure its very uniform distribution and good covering of the surfaces being treated; when wetting agents and adhesives are added to the working solutions, good retaining of the pesticides on the treated objects is ensured. Spraying depends to a smaller extent on the meteorological conditions. In addition, combined pesticide compositions can be used for spraying, which is virtually impossible in dusting.

The shortcomings of spraying include the complications involved in preparing the working compositions and in observing the preset rate of use of the liquid and the dose of the pesticide, and also spoiling of the apparatus as a result of corrosion and the use of a large amount of liquid, which makes treatment more costly.

For instance, in the surface treatment of orchards and woods, liquid is used at a rate of 2000 litres per hectare, and when treating field crops—400 to 500 litres.

Of special importance in aerial spraying is the homogeneity of the drops. Achievement of the optimal size of the drops is needed for reducing the losses of toxicants because of their drift under the action of eddy air currents and of evaporation.

Four main classes of drop dispersion are distinguished in aerial spraying: with an average drop diameter up to 50 μm—aerosol, from 51 to 150 μm—fine-drop spraying, from 151 to 300 μm—ordinary (medium-drop) spraying, and above 300 μm—large-drop spraying (Table 6).

In aerial chemical treatment, droplets of an aerosol size and small drops lend themselves to a greater extent to drift and evaporation, which is associated with the low initial velocity of their falling and the very small distance which they travel during their "lifetime".

According to G. Hartley (1967), a droplet of a 1% aqueous solution with an initial size of 50 μm already in a few seconds transforms into a more or less dry particle with a diameter of about 11 μm. Such dry particles are easily carried off by an air current and much more rarely settle on plants.

Table 6. Aerial Spraying (from "Instructions on Aerial Chemical Work", 1974)

Pesticides and objects	Rated consumption of liquid, litre/ha	Size of drops, μm	Density of drop network, No./cm²	Equipment
		I. Large-Drop		
Herbicides and highly toxic acaricides with systemic action	25 (low volume) 50 100 150	300	10-50	Aeroplanes AN-2, AN-2M, sprayers with section of 4×5, 5×5 mm; on helicopters, 1.25-2 mm
		II. Medium-Drop (Ordinary)		
Insecticides, acaricides, defoliants: on field crops in vineyards and orchards	50-100 200-400	151-300 151-300	20-70	Aeroplanes AN-2, AN-2M, sprayers with section of 2×5 mm; helicopters MI-1, MI-2, 3 mm with swirlers
		III. Fine-Drop Small-Volume		
Pentatomids, ordinary and gray weevils, corn weevils, frit flies, cereal leaf beetles, pea beetles, Colorado potato beetles, locusts, mangold flea beetles	25	51-150	70	AN-2, AN-2M, sprayers with section of 1×1 mm, MI-1, MI-2, with aperture diameter of 1.25-2 mm with swirlers
		IV. Ultrasmall-Volume (Supersmall-Volume)		
Insecticides, acaricides, herbicides, defoliants	Up to 5	50-150	60-100	AN-2, sprayers with section of 1×1 mm

The approximate values of the lifetime of drops of pure water at 15 °C and a relative air humidity of 40% are as follows:

Initial diameter, μm	Lifetime, s
50	4
100	16
200	63

The velocity of falling of a drop 200 μm in diameter in calm air is somewhat larger than 0.6 m/s, therefore when it falls from a height of 6 m, such a drop evaporates comparatively slightly.

A drop with an initial diameter of 100 μm begins to fall with a velocity of 0.3 m/s. Such a drop cannot reach the earth and evaporates half way down. A drop with an initial diameter of 50 μm drops in free fall by only 0.3 m and completely evaporates.

Drops over 200 μm in diameter may be directed onto fields being cultivated, while drops under 50 μm in diameter drift in virtually all conditions.

Fine-drop aerial spraying with rates of liquid consumption of 5-25 litre/ha is possible when pesticides are used in the form of oil emulsions and solutions.

Among the formulations suitable for fine-drop spraying are oil solutions of polychloropinene and HCH, mineral oil emulsions of these chemicals, parathion-methyl concentrate, and also concentrated solutions of some pesticides, for example an 8-15% solution of trichlorfon.

Fine-drop aerial spraying yields a good effect and substantially improves the productivity of such treatment.

According to the data of the Ukrainian board of civil aviation, in aerial treatments to control beet pests, the average productivity of an AN-2 aeroplane in conventional spraying of chemicals at a rate of use of the liquid of 50 litre/ha was 106.5 ha per flight-hour, in fine-drop spraying at a rate of 25 litre/ha was 157.4 ha per flight-hour, and when spraying at a rate of 5 litre/ha it was 213.3 ha per flight-hour.

A good way of reducing losses of a pesticide in aerial spraying as a result of drift and evaporation of the drops is the use of inverted emulsions in which oil is the dispersion medium, and the pesticide dissolved in water is the dispersed phase. An inverted emulsion has the consistence of a gel or paste. Consequently, when sprayed, it breaks up into rather large drops coated with a shell of non-volatile oil that do not evaporate in aerial spraying. In addition, the oil shell around the water drops promotes adhesion and retaining of the drops on plants. The drift of herbicides used in the form of inverted emulsions diminishes from two to three times.

Ultrasmall-Volume Spraying. Recent years have seen the conducting of studies in many countries that involve the use of ultrasmall-volume spraying with undiluted emulsifiable concentrates at a rate of from 1 to 5 litre/ha.

In comparison with small-volume spraying, ultrasmall-volume spraying increases the productivity of aerial treatment more than four times and substantially cuts the cost of the work.

The concentrates used for ultrasmall-volume spraying must have a fluidity at room temperature, a density of at least 1 g/cm^3, a low toxicity to mammals, a high biological activity.

They must be harmless to plants, and leave no persistent residues.

In connection with the use of ultrasmall-volume spraying, our notions of the effective size of pesticide drops have changed. It was found that an insecticide in the form of fine drops is considerably more toxic than in large ones. The explanation is that a multitude of fine drops getting onto insects and having the same overall volume as one large drop come into contact with a considerably larger area of the insects' integuments, therefore the lethal dose of the insecticide penetrates more rapidly through the cuticle.

The American experience of ultrasmall-volume aerial spraying of large territories populated by blood-sucking flies from a height of several hundreds of metres deserves attention. The operating width in this case increases to 1.5-3 km.

Ultrasmall-volume spraying is superior to other kinds of treatment in its effectiveness, which is explained by the more prolonged action of the technical insecticide in comparison with diluted emulsions.

In addition, in ultrasmall-volume spraying, no preliminary preparation of the solutions and emulsions is needed, which diminishes the contact of the workers with the toxicants.

At present, special insecticides for ultrasmall-volume treatment are being prepared and tested. Among them are: ritsifon—a 30% solution of neutral trichlorfon, malathion—a 40% solution of malathion in ethyl cellosolv, dilor—a 15% solution in nephitocide oil, and 70% formothion.

In surface treatments, three kinds of spraying are distinguished: large-volume, small-volume, and ultrasmall-volume (Table 7).

Large-volume spraying is used in the following cases: when the pesticide is phytocidal in increased concentrations, exhibits only contact action, and requires abundant wetting of the plants, is highly toxic to humans, and is allowed to be used when greatly diluted (knapsack sprayers) on small areas and for treating individual trees. Higher rates of use of liquids are also needed when working with fungicides.

Dusting is the application of dust formulations to the surface of plants or insects with the aid of special apparatus. A merit of this way of using pesticides is its simplicity. Special compositions do not have to be prepared directly before work because ready dusts are available. In addition, pesticides in the form of a dust cover dense cereal crops very well.

Dusting, however, also has appreciable shortcomings. They are expressed in the high dust content of the air in the working zone, which is dangerous to the workers, in the high rate of use of the formulation, and also in the drift of the dust cloud with the wind currents, and washing off by rain.

Dust formulations often drift over large distances, which may have undesirable consequences. Drift occurs because the dust particles slowly settle in the air and are caught up by the eddy currents.

Table 7. Kinds of Spraying According to the Amount of the Working Liquid (When Controlling Pests)

Crop	Rate of use, litre/ha	Size of drops, μm	Apparatus
	Large-Volume Spraying		
Field (sugar beets, potatoes, etc.)	400-600	120-300	Boom sprayers
Berry patches and grapevines	1000-1500	120-300	Ditto
Orchards with an age of:			
8-10 years	500-650	120-300	Booms sprayers with fire-hose nozzles
10-12 years	1000	120-300	
12-16 years	1200	120-300	
16-20 years	1500-2000	120-300	
	Small-Volume Spraying		
Field crops	80-135	20-70, not over 100	Boom sprayers with reduced openings of atomizers
Ditto	15-50	Ditto	Blower sprayers
Berry patches and grapevines	200	Ditto	Boom sprayers
Orchards	250-500	Ditto	Ditto
	Ultrasmall-Volume Spraying		
Various plantings	0.5-2	60-100	Special sprayers

A glance at Table 8 shows that the magnitude of the drift is especially great for particles 25 μm in size falling from a height of 10 m. Particles 100 and 200 μm in size drift over an insignificant distance, especially when the height of falling is 5 m.

Table 8. Dependence of Drift of Particles on Their Size and the Height of Falling

Diameter of particles, μm	Drift of particles (m) when falling from a height of	
	5 m	10 m
25	179.2	358.4
100	11.2	22.4
200	2.8	5.8

To improve the quality of dusting, especially in aerial treatments, and reduce the drift, up to 3-5% of bonifiers are added to dusts.

They are mineral oils that promote the aggregation of the finest particles into larger lumps which settle better in dusting.

It must also be noted that sharp-edged particles are retained better on the surfaces of leaves, whereas spherical ones roll off. This is why carriers obtained by grinding meet this requirement better.

Pesticides formulated as dusts are retained better on wrinkled, fluffy, and horizontally arranged leaves. The quality of spraying depends to a large extent on the time when it is performed; it is preferable to do this early in the morning or in the evening in the absence of ascending streams of air, in still and calm weather, over dew or after rainfall, when the leaves are wet.

Fumigation, or gassing, involves the decontamination of objects from insects, their larvae and eggs, mites, nematodes and other pests by fumigating them with vapours or gases of poisonous substances. The pesticides used for this purpose are called **fumigants.**

Fumigation is one of the most widespread ways of controlling pests of reserve supplies in storage and transportation, pests and diseases in sheltered ground, pests and diseases of planting stock, and also valuable citrus crops and tea. Fumigation is widely used to control pests and rodents dwelling in the soil.

Fumigation is a very effective method because the poisonous vapours or gases together with the air penetrate very well into various porous materials, cracks, and the most minute openings in which harmful organisms may nest. With good sealing of the object, the observation of proper fumigation techniques, and the required exposure, a 100% decontamination effect can be obtained.

The effectiveness of fumigation and the technique followed in performing it depend on the properties of fumigants and first of all on their state of aggregation (liquid, gas, or solid).

The most important properties of fumigants are their volatility, rate of evaporation, the diffusion of the fumigants in air, their liability to explode or ignite, the degree of sorption by various objects, their action on metals and other materials, toxicity, and degasability.

The volatility is characterized by the maximum amount of vaporous fumigant contained at a given temperature and pressure in unit volume of air. It is expressed in mg/litre or in g/m^3 of air and grows with an increasing air (fumigant) temperature (see Table 9).

The volatility increases when the pressure of the air drops, which is taken advantage of in vacuum fumigation in chambers.

The rate of evaporation of a fumigant is determined by the volume of the vapours evaporating from an area of 1 cm^2 in one minute. The rate of evaporation increases with elevation of the air temperature and a growth in the open area. Consequently to rapidly obtain the required fumigant concentration in the premises being gassed, which is lethal to the harmful organisms, the fumigant or the room itself

Table 9. Volatility of Selected Fumigants Depending on the Temperature (After P. Popov)

Fumigant	Temperature, °C	Volatility at 760 mm Hg, mg/litre (g/m^3)	Fumigant	Temperature, °C	Volatility at 760 mm Hg, mg/litre (g/m^3)
Dichloroethane	10	205	Chloropicrin	10	96
	20	330		20	165
	30	509		30	271

is heated, while liquid fumigants are poured into flat pans or sackcloth is wetted with them and hung up in the premises being gassed to increase the evaporating surface.

The improvement in the effectiveness of fumigation, especially of loose materials with a large volume of coarse and fine pores, depends directly on the rate of diffusion of the fumigant in the air and, consequently, on its penetrating ability. The rate of diffusion of a fumigant in air increases with elevation of the temperature and depends on the vapour pressure. The higher the vapour pressure of a fumigant, the more rapidly does it diffuse in the air. For example, the vapour pressure of hydrocyanic acid at 25 °C is 760 mmHg and its volatility is 1100 g/m^3, whereas the vapour pressure of chloropicrin at this temperature is only 18.3 mmHg and its volatility is 165 g/m^3; this explains the lower diffusion of its vapour in the air and its lower penetrating ability.

The penetration of fumigant vapours into the body of objects being decontaminated can be accelerated by raising the temperature and by using vacuum chambers and other technical contrivances.

Of great danger is the ability of fumigants to ignite or explode when a definite concentration of the vapours or gases in the air is reached. The zone of the explosive concentration, i.e. the zone between the lower and upper limits of the ignition concentration, changes in some fumigants within a broad range of concentrations. Such fumigants are especially dangerous. Therefore, when working with them, all possible sources of ignition must be isolated.

Of major significance in fumigation is the sorption of the fumigant by the material being decontaminated. We distinguish **adsorption** —concentration of a fumigant at the surface and its sorption by the surface layers, **absorption** of the fumigant by the entire mass of the material being decontaminated, and **chemisorption**—the chemical reaction of the fumigant with the substances and objects being decontaminated.

Sorption results in an increased consumption of the fumigant, hinders subsequent degassing (desorption), and residual amounts of

fumigants exceeding the tolerance levels may accumulate in products.

Sorption grows especially in the fumigation of agricultural products and materials with a large overall surface (flour, cereals, combined fodder, and the like).

Among fumigants, chloropicrin is sorbed the most and persists for a long time in the materials being fumigated. Methyl bromide has a high penetrating ability, but is sorbed very weakly and is well degassed. This explains its use for the gassing of fresh fruit, including citrus fruit, and dried fruit.

Work with fumigants is performed by fumigation teams with observance of measures of personal and public safety.

All fumigants are sharply toxic to warm-blooded animals and humans.

To identify fumigants that cannot be determined according to their odour or irritating action, signalizers are added to them. These are substances that either have a recognizable odour or cause irritation of the mucous membranes or lacrimation (lacrimators).

The main kinds of fumigation work are as follows.

Fumigation of premises (stores, elevators, granaries, grain, etc.). The fumigation is preceded by preparatory work: the volume to be treated is determined, the premises are sealed; when required and when working with non-flammable fumigants, the premises are heated (by firing furnaces); all objects that might be damaged by the fumigant are removed from the premises; when using flammable fumigants, the safety from fires is ensured.

The gassing of prepared premises is performed by spreading out a solid fumigant in a thin layer, pouring liquid fumigants into pans, spraying a liquid fumigant, hanging up pieces of fabric impregnated with fumigants, and also by filling the premises with a fumigant from cylinders. In addition to these passive ways of fumigation, fumigants are introduced into the premises being treated with the aid of type 2-AG and 2-AGM apparatuses. In these apparatuses, liquid fumigants evaporate to form a vapour and air mixture which is fed under pressure into the premises being treated and penetrates very well into the mass of the material being fumigated.

It is especially important in fumigation to establish the duration of gassing—the exposure, because many harmful organisms can live for quite a long time in a poisoned atmosphere with closed spiracles at the expense of the oxygen contained in their tracheal system, and they will perish only after all of this oxygen is used up. It has been established that a small addition of carbon dioxide to fumigants may stimulate the respiratory movements and opening of the spiracles in insects and, consequently, may increase the toxic action of the poison.

After fumigation, the premises are degassed by ventilation, and when necessary, by using chemicals neutralizing the fumigants.

Grain is degassed by passing it through grain cleaners, driers, by active ventilation, and by transportation on conveyors.

Chamber Fumigation. Seeds, fruit, bulbs, and various planting stock are decontaminated in chambers where good sealing, temperature control, and precise dosing of the fumigant are ensured.

Non-vacuum and vacuum fumigation are distinguished. The former is performed like the fumigation of premises.

Non-vacuum chambers are conventional, well sealed rooms into which the products are placed and the required fumigant concentration is created in them.

For example, non-vacuum chambers with a volume from 40 to 200 m^3 are used in nursery farms to decontaminate planting stock (seedlings of various cultures, flower bulbs) from quarantine blight and other pests. The products are loaded into the chambers in open containers on carriages.

Various non-standard premises are also used for chamber fumigation—adapted storerooms, refrigerator premises, the holds of ships and barges, tankers, railway cars, etc.

Vacuum chambers have special equipment for evacuating the air after the products have been placed in them. A vacuum pump is used to pump the air out of the chambers, and the pressure in them is lowered to 112-125 mmHg. Next gas producers deliver a gaseous or vaporous fumigant into the chamber that penetrates into the material being treated at a high rate of diffusion. After gassing, the poisonous air is pumped out and passed for neutralization through an absorber, and the chambers are filled with clean air. After sufficient ventilation, the products are discharged from the chamber.

Standard vacuum and non-vacuum chambers are provided with means for sampling the gas and air mixture to determine the concentration of the fumigant vapours.

The equipment of fumigation chambers includes gas-evaporating installations by means of which the fumigant is fed into the chambers only in the gaseous state, gas analysers for determining the concentration of the fumigant vapours and the completeness of degassing of the material, and halogen indicator burners for controlling the purity of the air at workplaces and monitoring leakage of the fumigant vapours from the chamber at the working joints.

Persons attending to a fumigation chamber are provided with gas masks.

Tent fumigation is employed for exterminating pests on especially valuable trees and shrubs. In this method, the trees or shrubs are covered with a tent made from a gasproof fabric, and the fumigant is introduced under the tent in the required concentration. Hydrogen cyanide is used most often for this purpose.

Greenhouse fumigation is a widespread way of decontaminating sheltered soil structures. This method is virtually the same as the

fumigation of other premises, but the fumigants are chosen with a view to their action on vegetating plants if the latter are present during the fumigation. The aerosol method of fumigating greenhouses is also used.

Fumigation of the soil is performed to kill soil-dwelling pests. When fumigating soil, account must be taken of its high absorptivity, and also of the difficulty for fumigants to penetrate into it, especially into dense soils of a heavy mechanical composition, and into soils containing excessive moisture. In addition, fumigants evaporate rapidly from soils.

With a view to these features, substances with a higher boiling point and, consequently, less volatile are used for soil fumigation. They are incorporated to a depth of 18-20 cm and deeper, and the soil is mulched from the surface. Solid fumigants can be introduced into furrows with incorporation into pits made by steel rods. Liquid fumigants are incorporated to the required depth by means of injectors.

Sometimes tier fumigation is used with introduction of the fumigants in tiers to a depth of one metre.

Aerosols. Aerosols are defined to be suspensions of fine droplets of a liquid or solid particles of pesticides in air. Aerosols consisting of liquid particles form mists, and of solid ones—smoke. The diameter of the aerosol particles ranges from 0.001 to 50 μm.

Aerosol particles settle in air very slowly (data of P. Popov):

Diameter of water drops, μm	100	10	0.1
Speed of settling of water drops in air, cm/s	120	1.2	0.00012

The optimal size of aerosol particles ranges from 20 to 50 μm. Aerosol particles carry an electrical charge, positive or negative, which depends on the nature of the substance.

Aerosols are prepared by the dispersion and condensation methods. In the dispersion method, the liquid pesticide is comminuted with the aid of special aerosol generators by a highly pressurized air stream, or the pesticide is dissolved in a volatile liquid which is then sprayed—the liquid evaporates and the drops acquire the size of aerosol particles.

In the condensation method, a liquid pesticide is evaporated by heating, and the vapour formed condenses in air to produce solid or liquid aerosol particles. This is achieved by the use of aerosol generators and a fire tube.

The simplest way of obtaining aerosol smokes is to burn various compositions containing pesticides, for example pesticide paper. The latter is prepared from conventional filter paper by impregnating it with a 5-7% solution of saltpetre and a concentrated solution of the pesticide in a solvent.

Aerosols are widely used for controlling orchard pests, for the disinsection of granaries and stores, greenhouses, and other premises.

Depending on what they are used for, aerosols must have the following optimal dispersity:

when treating premises with pesticides having a fumigating action (chloropicrin, lindane, etc.), the mean size of the droplets must not exceed 5 μm (a dispersity range of 0.5-10 μm);

when exterminating flying insects, the mean size of the droplets is 20 μm (a dispersity range of 10-30 μm);

for adequate deposition of the toxicant on vegetation—not over 40 μm (a dispersity range of 20-50 μm);

in fine-drop spraying—not over 100 μm (a dispersity range of 50-150 μm).

The shortcomings of aerosols diminishing the effectiveness of their use in a number of cases include the drift of the mist in wind currents, in ascending air streams, the poor settling of the most minute aerosol particles, and also their poor penetration into porous materials and cracks.

Poisoned baits are widely used for controlling rodents and also many insects.

Baits are mainly prepared from poisons with stomach action and food liked by the rodents and insects. The consumption of toxicants for preparing poisoned baits is minimum in comparison with the other ways of using pesticides.

Grain, cereals, flour, chaff, cake, etc. are used as the baiting material that is mixed with the toxicants.

Moist poisoned baits are prepared by impregnating the baiting material with a solution or suspension of the poison.

Semidry poisoned baits contain less moisture because the baiting material is dried slightly after treatment with the solution or suspension of the poison.

Dry poisoned baits are prepared by mixing the bait material with a powder of the toxicant. Adhesives—mineral oil, paste, etc.—are added to the baits. Dry baits are also prepared by drying moist or semidry poisoned baits.

The **treatment of seeds and planting stock** is performed for protecting them and plant seedlings from being damaged by rodents and soil-dwelling insects or larvae, and also for destroying pathogens of plant diseases. For this purpose, combined protectants are used that contain both systemic and contact insecticides.

Modern seed protectants have a broad spectrum of action; a number of pesticides can penetrate into a plant being protected and suppress a deeply lying infection.

The following is achieved in the treatment of seeds of agricultural crops:

decontamination of seeds from pathogens of plant diseases transmitted through them (seed treatment makes it possible to control loose smut and common bunt of wheat, loose and covered smut of barley, flag and covered smut of rye, loose and covered smut of oats, loose smut of millet, to diminish the harm caused by fusarial wilt, helminthosporiosis, and bacteriosis of cereals, black root of sugar beets, bacterial blight of cotton, root rot and ascochitosis of small grain and bean crops, pyriculiariosis and root rot of rice, sclerotinosis of sunflowers, etc.);

retaining of the planting properties of seeds in storage and protection of planted seeds and shoots from growing mouldy in the soil;

reducing the damage to seedlings by soil-dwelling pests;

increasing the energy of seed sprouting and their field germination rate;

stimulating the growth and development of plants;

improving the wintering of winter crops, which ensures a normal density of the shoots and an increase in the harvest.

Depending on the kind of pesticide and also in accordance with the biology of the pathogen, dry, semidry, and moist treatment are used. Moist treatment has a restricted use. In dry treatment, powdered formulations are mixed with the grain. This method has appreciable shortcomings: the sanitary conditions of work become worse because of an increased dust content in the air, this being attended by a growth in the losses of the formulation, in addition, the formulations are retained poorly on dry seeds.

The shortcomings of dry treatment can be eliminated when using aqueous solutions of pesticides for decontamination of seeds, or with the simultaneous moistening of the seeds and the powder in the course of treatment. In the treatment of seeds with suspensions of powdered formulations, the rate of use of the liquid is 10-15 litre/tonne. The dose of the formulation remains the same as in the dry method of treatment, but it is difficult to prepare a homogeneous suspension. This is why it is better to use treatment with moistening.

To improve the effectiveness of treatment and the sanitary conditions of work, various adhesives should be used: liquid sulphite and alcohol slops (0.7-1 kg/tonne), a concentrate of solid slops (0.5-0.7 kg/tonne), and silicate glue (150-200 g/tonne).

When treating sugar beet seeds, it is good to use liquid slops as the adhesive (3 kg/tonne). Sugar beet seeds are treated in type APS-4 machines.

When the seeds of grain crops are being treated with moistened formulations or suspension of ethylmercury chloride, thiram, or carboxin together with a growth promoting substance, water is replaced with an aqueous solution at a rate of 4-6 litres of a 60% solution of the growth promoting substance per tonne. Water is

added up to 10-15 litre/tonne. The rate of use of the protectant is not changed.

Semidry treatment of barley and oat seeds is performed with a 1.25% solution of 40% formalin (0.5% relative to the active ingredient). The rate of use of the working formalin solution is 30 litre/tonne for oats and 15-20 litre/tonne for barley. After being wetted, the seeds are held under a canvas for three or four hours. Greatly infected millet seeds are decontaminated with a 0.33% solution of 40% formalin (0.11% relative to the active ingredient), with 100 litres of the working solution being used per tonne of seeds.

A solution of such a concentration is suitable for decontaminating only one batch of millet seeds, after which holding under a canvas for two hours is obligatory.

Formalin is to be used for treatment only prior to sowing. The presowing storage period of treated seeds is five days.

Treated seeds of sugar beets, flax, corn, vegetable crops, and cotton at their conditioned moisture content can be stored for several years. The seeds of all agricultural crops brought up to sowing conditions may be treated in good time.

The treatment of seeds of pod cultures with ethylmercury chloride in good time is especially effective against smut diseases. To increase the effectiveness of controlling covered and loose smut of pod cultures, the seeds are treated not later than two or three weeks before sowing with moistening and the use of adhesives. Mercury toxicants used to treat seeds with a moisture content over 16% upon prolonged storage after treatment may cause lowering of germination and deformity of the shoots. Wheat, oat, and barley seeds with an increased moisture content may be treated with ethylmercury chloride only as an exception, and not earlier than three days before sowing.

When oat and barley seeds were not treated in good time, they are processed with formalin in the semidry way not earlier than 3-5 days before sowing.

Freshly harvested seeds of winter crops should be subjected to air and heat processing and dried to the conditioned moisture content prior to treatment.

When winter wheat is infected with common bunt, and winter rye with flag smut, and also when wheat seeds are infected with fuzariosis and helminthosporiosis and with their increased moisture content, it is good to treat them with formulations based on thiram in the conventional doses.

Seeds intended for processing with bacterial fertilizers should be treated with toxicants of the mercury group or thiram in good time, 20-30 days before bacterization. In treatment with systemic fungicides (benomyl), nitrogenation may be performed simultaneously.

In all cases, sealed worm and chamber treating machines should be used for treatment.

Special Part

Chapter 6

MEANS FOR CONTROLLING PLANT PESTS

6.1. Insecticides and Acaricides

According to an estimate of experts of the United Nations Food and Agricultural Organization, at present the world's agriculture loses about one-third of what it produces every year as a result of the activities of harmful organisms, 13.8% of all losses falling to the share of insects and mites. The harm produced by insects and mites is expressed in both the direct damage to plants and food products (the gnawing and eating of leaves and fruits, defoliation, the yellowing and dying off of plant parts) and in their indirect damage (the creation of conditions for the development of diseases, the vectoring of pathogens, spoiling of the quality of products, etc.). About 70 000 species of insects and mites attack all the parts of agricultural plants during their entire period of vegetation and in storage, and about 10 000 species of them cause a substantial economical harm. Pests such as locusts are a real calamity to many agricultural countries, destroying crops completely in some years.

The diversity of the species and harmful forms of insects and mites, the features of their structure, biology and ecology (such as the thick protective integuments, the high vitality, fertility, and adaptability to new conditions, the large number of generations in a single season, and the diversity of their habitats) considerably hamper the control of insects and mites and the development of effective chemical means of protection against them. Insecticides with a stomach action that are effective in controlling leaf-eating pests have no effect on sucking insects and mites, and, conversely, systemic insecticides intended for controlling the latter hardly affect leaf-eating insects. Compounds with contact action have a rather broad control spectrum, but harm the beneficial entomofauna to a great extent. All these circumstances determine the broad range of insecticides and acaricides used in agriculture and the large amounts in which they are applied.

Chemical substances are being used for controlling insects from time immemorial. Homer (1000 B. C.) mentioned the use of sulphur as a repellant of insects; Alinii (70 B.C.) reported the use of arsenic as a means for killing insects. In 1867, copper salts of arsenic acids were used in Europe to control the Colorado beetle. The beginning of the

Table 10. Classification of Insecticides Used in the USSR

Classes of chemical compounds	Mode of insecticide action		
	contact or contact-stomach	stomach or stomach-contact	systemic or systemic-contact
I. Inorganic substances			
II. Organic compounds			
1. Organochlorine substances (chlorinated hydrocarbons):			
(a) hexachlorocyclohexane and its analogues	Lindane		
(b) polychloroterpenes	Toxaphene, polychloropinene		
(c) polychlorocyclodienes	Heptachlor, dilor, despirol, endosulfan		
2. Derivatives of carbamic acid	Carbaryl		Pirimicarb
3. Organic compounds of phosphorus:			
(a) derivatives of phosphoric acid	Dichlorvos	Tetrachlorvinphos	Metasystox
(b) derivatives of phosphorothioic acid	Pirimiphosmethyl, bromophos, fenthion, phoxim, parathion-methyl, trichlorometafos-3, cyanophos		
(c) derivatives of phosphorodithioic acid	Malathion	Phosalone Phosmet, phenthoate	DAEP, formothion, diazinon, menazon, dimethoate
(d) derivatives of pyrophosphoric acid			
(e) derivatives of phosphonic acids	Trichlorfon		
4. Nitrophenols	DNOC, nitraphen		
5. Hydrocarbons:			
(a) petroleum oils	Mineral oils, formulations No. 30, 30A, 30C, 30CC, 30M, petroleum-oil emulsions		
III. Insecticides of a vegetative origin			

twentieth century was characterized by the development of fumigation and the manufacture of formulations based on nicotine, while 1925 saw the appearance of the first synthetic organic formulations from the group of nitrophenols. But these insecticides did not come into great favour for a number of reasons (the narrow specificity of their action, the high toxicity to humans and animals, the high cost of protective measures, and so on).

A real revolution in the chemical protection of plants was made by the appearance in the early 1940's of contact insecticides from the group of chlorinated hydrocarbons (DDT, HCH, aldrin, etc.) that were distinguished by their exceptionally broad spectrum of action, high activity, and cheapness of manufacture. In 1946, the commercial production was commenced of insecticides and acaricides from the group of organic compounds of phosphorus, among which there were later discovered systemic toxicants having a sufficient selectivity.

Modern insecticides and acaricides belong to different classes of chemical compounds and have a different mode of action (Table 10). Synthetic organic compounds predominate among them, especially derivatives of phosphoric, phosphorothioic, and phosphorodithioic acids. Basically, the representatives of the same class are characterized by common specific properties and a single mechanism of their action on an organism. It is therefore more convenient to study the properties and features of these substances by classifying them according to their chemical structure.

6.1.1. Organochlorine Compounds

This group of insecticides includes substances varying in their chemical structure. But the common nature of some of their properties (a high insecticidal activity, chemical and biological persistence) makes it possible to combine them into one group.

All organochlorine insecticides are poorly soluble in water and well soluble in organic solvents, including fats. Many of them are quite volatile.

They are thermally and chemically stable substances withstanding the action of various factors of the environment (temperature, solar radiation, moisture, etc.). This underlies the prolonged protective action of these substances against pests, but at the same time creates a danger of contaminating the environment and agricultural products.

Representatives of this group persist in the soil from 2 to 15 years, remaining for a long time in the top layer and slowly migrating along the soil's profile. These insecticides penetrate from the soil into plants, especially into root vegetables, and also into ground water and water basins. Organochlorine compounds incorporated into

the soil in large doses may inhibit nitrification processes for 1-8 weeks and suppress its general microbiological activity for a short time. They do not substantially affect the properties of the soil, however.

Organochlorine insecticides that get into water are detected in it for several weeks or months, being simultaneously absorbed by aqueous plants and animal organisms and accumulating in them.

The use of these pesticides in agriculture is attended by their getting into the atmosphere. The duration of detecting their vapours and aerosol particles in the air, as a rule, does not exceed several days, but subsequently the vapours of these toxicants and their particles reenter the air when the temperature rises and when the soil is cultivated, which is a hazard to persons working in the treated fields.

Organochlorine compounds decompose very slowly in plants and on the surface (after a single treatment, their residues are detected in 30-75 days, while their entry through the roots continues during the entire vegetation period). The residues of these compounds are not removed from agricultural products during thermal or culinary processing. All organochlorine compounds have no negative action on the plant being protected in the recommended concentrations, and many of them even stimulate the growth of plants.

The representatives of this group are mainly contact insecticides with prolonged residual effects and a broad spectrum of action. Organochlorine insecticides upon entering an insect's organism act on its nervous system, violating, as is assumed, the lipoid equilibrium of the nerve cell membranes, and preventing the transmission of nerve impulses. Insects perish as a result of malfunctioning of their nervous system, attended by tremors and paralysis.

The process of poisoning, however, is quite protracted and may continue up to seven days.

The metabolism of chlorinated hydrocarbon derivatives in the organism of an insect, and also of other living beings, occurs in three main directions:

(1) dehydrochlorination with the detachment of one or more HCl molecules and the formation of products with a low toxicity;

(2) oxidation to epoxides and other no less toxic metabolites (activation);

(3) hydrolysis to water soluble substances that are easily excreted from the organism.

The selectivity of a compound and its toxological properties depend on the direction of the metabolism processes.

The perennial use of organochlorine compounds leads to the appearance of resistant insect populations, and acquired group resistance appears.

Most substances of this group are moderately toxic to humans and animals, and only a few are highly toxic (Table 11).

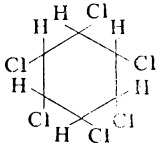
Table 11. Acute Toxicity and Threshold Doses in the Chronic Testing of Organochlorine Compounds on Rats

	Hexachlorocyclohexane				Hepta-chlor	Endo-sulfan	Toxa-phene	Dilor
	gamma isomer (lin-dane)	tech-nical	alpha isomer	beta isomer				
Oral dose for test animals LD_{50}, mg per kg of live mass	125	600	500	>6000	90	45	< 200	2000
Threshold dose in 2-year chronic ingestion tests, mg per kg of food	25-50	10	10	< 10	< 1	30	1.2	

The dermal toxicity in the main is not high, but many compounds have an irritating action on the skin and mucous membranes.

A characteristic and very negative property of organochlorine substances is the pronounced and sharply pronounced ability of material cumulation (groups I and II of the sanitary classification). Their threshold doses in chronic tests do not exceed 50 mg per kg of food (see Table 11). The repeated ingestion of small amounts of these toxicants into an organism facilitates the development of chronic poisoning. This sharply restricts the possibility of using organochlorine compounds on a large scale. At present, hexachlorocyclohexane, toxaphene, polychloropinene, heptachlor, endosulfan, dilor, and despirol are allowed to be used in agriculture in the USSR.

HCH (Hexachlorocyclohexane, Hexachloran)

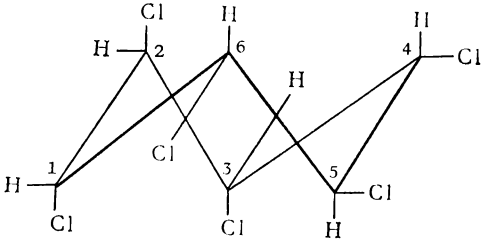


The active ingredient, 1, 2, 3, 4, 5, 6-hexachlorocyclohexane*, may be in the form of one of several stereoisomers having a different orientation of the C—Cl bonds and a different distribution of the hydrogen and chlorine atoms along them. The atoms 1, 3, and 5 are in one plane,

* This substance is sometimes called benzene hexachloride (BHC)— a misnomer—and is marketed in some countries by this name—*Translator's note*

and 2, 4, and 6, in another one. The bonds of the carbon atoms with the other atoms and groups may be at right angles to the indicated planes or at an angle of 109°28′, to the periphery of the molecule. The properties of the substance depends on how the C—Cl bonds are oriented.

At present 11 stereoisomers of hexachlorocyclohexane are known. Among them, only the gamma isomer—lindane (gammexane, gamaphex) has a high insecticidal activity. The C—Cl bonds at the atoms 1, 2 and 3 in this isomer are at right angles to the plane, and at the atoms 4, 5, and 6—at an oblique angle to it:



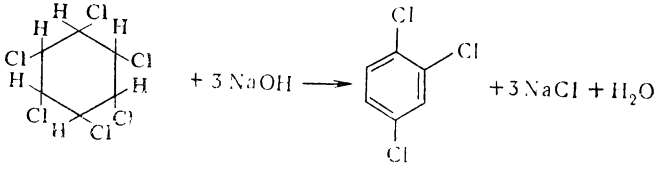
Physical and Chemical Properties. All the isomers of hexachlorocyclohexane are crystalline substances with a bitter taste and with no odour. They differ considerably in their physical properties. The melting point of lindane is 112.9 °C. It is thermally stable, but at high temperatures volatilizes with the formation of a dense white smoke, which allows it to be used in the form of an aerosol. Hexachlorocyclohexane decomposes only slightly under the action of ultraviolet radiation, but owing to its relatively high volatility (1.8 mg/m^3 at 30 °C), it evaporates quite rapidly from treated surfaces or volatilizes with water vapour. This is why its persistence depends mainly on the temperature.

Lindane dissolves very poorly in water (10 mg/litre at 20 °C), and well in benzene, ethyl and methyl alcohols, ether, acetone, and also in fats and fatty oils.

HCH is very stable to the action of various oxidizing agents and concentrated acids (sulphuric, nitric, hydrochloric) even at the boiling point of the latter. This property is taken advantage of when analysing plants for their content of insecticide residues: the plant sample is burned with sulphuric acid, after which the HCH is easily recovered by evaporation with water vapour.

Under the action of alkalies, hexachlorocyclohexane decomposes with the detachment of hydrogen chloride and the formation of trichlorobenzene, mainly 1,2,4-trichlorobenzene, which is not toxic

to insects:



Consequently, it is not recommended to use this toxicant together with lime or with pesticides having an alkaline reaction.

Persistence in Soil. In connection with the high thermal and chemical stability of the hexachlorocyclohexane isomers, they decompose slowly, and persist in the soil for three or four years on an average. Upon perennial application, the content of its residues in the soil ranges from tenths of a milligram to several milligrams per kilogram of soil. The persistence of HCH in the soil depends on the rate of use of the formulation, the kind of soil, temperature, pH, and the microbiological activity. It persists for a longer time in soils with a high content of silt or humus than in poorly adsorbing soils. With elevation of the soil's temperature, the toxicity of HCH to insects grows, but the duration of its action and its persistence diminish. For example, at 55 °C, a loss of toxicity is noted in four hours. The processes of decomposition of the toxicant accelerate, and its effectiveness drops with an increase in the soil's pH. This is why heptachlor is used to control soil-dwelling insects in the southern regions of the USSR with their high summer temperatures and with their alkaline soils.

Notwithstanding its low solubility in water, hexachlorocyclohexane can migrate along the soil's profile to a depth of up to 60 cm and penetrate into the ground water.

In its recommended doses, hexachlorocyclohexane does not have a negative effect on the population of microorganisms in the soil and on the processes occurring in it. In tests with pure cultures, however, lindane suppressed the development of bacteria such as *Azotobacter sp.*, *Nitrosomonas sp.*, *Bacillus megaterium*, and of some species of fungi: *Aspergillus fumigatus*, *A. terreus*, *Penicillium sp.*, and *Fusarium oxysporium.*

Lindane in doses exceeding 100 mg per kg of soil suppresses the processes of respiration and mineralization of organic matter. Introduction of this toxicant into the soil is followed by temporary inhibition (up to three weeks) of the nitrification process. In tests on paddy fields, it was shown that with a dose of lindane of 20 mg/kg the losses of nitrogen diminish owing to the suppression of denitrification.

The activity of anaerobic microorganisms (*Escherichia coli*) and green algae is of great importance in eliminating HCH from the soil. It has been established that the decomposition products contain

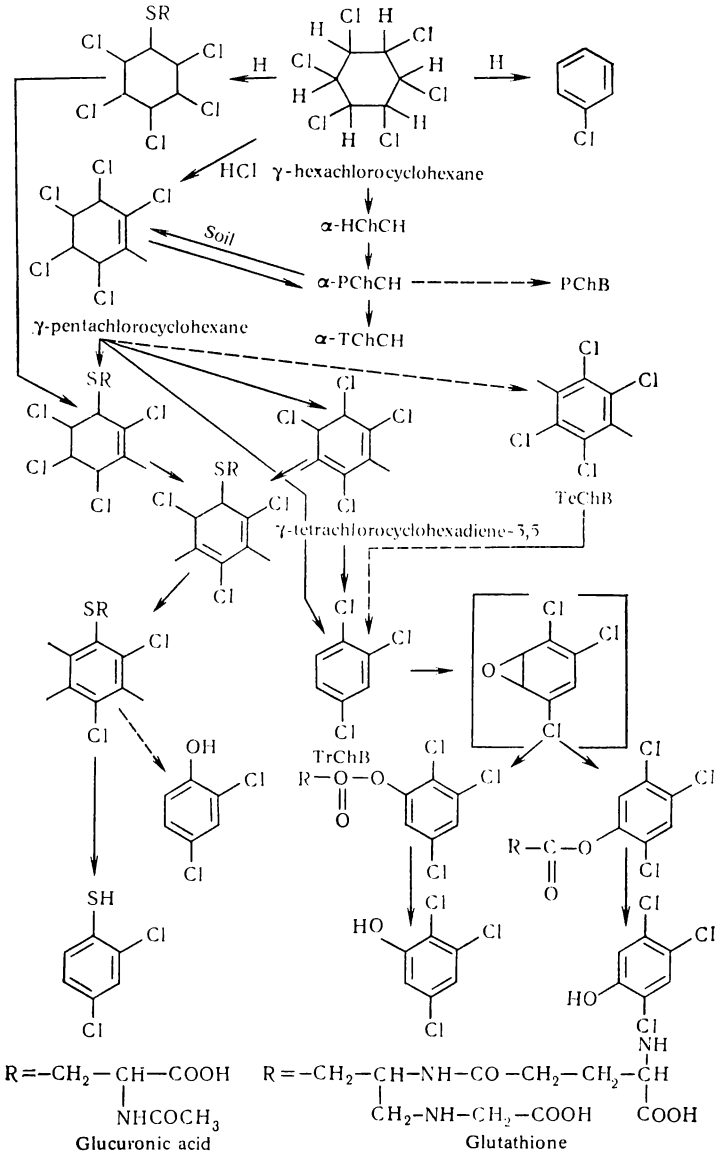


Fig. 3. Diagram of metabolism of γ-hexachlorocyclohexane (lindane)

gamma and alpha pentachlorocyclohexenes, penta- and tetrachlorobenzenes (see Fig. 3). With the participation of *Pseudomonas putida*, the lindane in the soil is isomerized to alpha-HCH with the loss of its insecticidal activity.

Action on Plants. Lindane penetrates into a plant through its leaves and roots, and is capable of migrating along the plant tissues and accumulating in them in a considerable amount.

The lindane content depends on the dose used, the kind of plant, the ways of entry, the kind of soil, and the meteorological conditions.

After treatment of the green parts, the amount of lindane in plants rapidly diminishes, and in 20-40 days, depending on the dose, drops to 1/10-1/30 of the initial amount (up to 0-0.4 mg/kg). The toxicant enters a plant through its roots considerably more rapidly and in larger amounts. Owing to the prolonged persistence of the substance in the soil, its entry into plants continues for a long time. In light sandy and sandy loam soils, the amount of lindane entering plants is considerably higher than in heavy and peaty soils. When the moisture content of the soil grows, this process also increases. Getting into fruits and vegetables, HCH imparts an unpleasant odour and taste to them. This occurs even with a very low content of the substance in them (of the order of 0.1 mg/kg). When the toxicant is incorporated into the soil, an especially strong specific taste is acquired by root vegetables, potatoes, and berries.

HCH formulations applied at the recommended rates do not cause burning of plants or suppression of their growth. After treatment of plants, changes in their metabolism are noted: a temporary (7-10 days) increase in hydrolytic processes, and an increase in the content of simple sugars and aminoacids without a substantial suppression of synthesis processes. Later, the growth of the plants returns to normal or is even stimulated. A definite stimulation of the growth of plants is observed after seed treatment. An increase in the rate of use of HCH, however, causes distortion and deformation of the seedlings, stopping of the growth of the primordial roots and of the expansion of the branch roots.

The prolonged storage of treated seeds may lead to a decrease in their germination.

Action on Insects. Lindane is a highly active insecticide with mainly a contact and stomach effect.

At a dose of 0.1 $\mu g/m^2$, the contact effect manifests itself already in a few minutes after the insecticide gets onto an insect. Owing to the high vapour pressure, it has the properties of a fumigant. After being incorporated into the soil, the insecticide penetrates into a plant, exhibits a systemic effect, and protects seedlings from pests for 5-15 days. It acts on some insects as a repellent.

Lindane is a poison affecting the nervous system. It penetrates rapidly through the integuments of insects and with the stream of

hemolymph or directly reaches the nervous system, concentrating in the peripheral regions of the ganglia of the cephalic and abdominal parts. The affection of insects begins with excitation, which is rapidly followed by the loss of coordination of movements. Next paralysis of the extremities sets in, and soon general paralysis. The last stage may last from a few hours to several days.

Poisoning by lindane is attended by a sharp increase in the intensity of respiration, disruption of the process of acetylcholine synthesis, and histological changes in the hemolymph cells (an increase in the number of multinuclear cells, decomposition of the protoplasma and then the nuclei of cells). These processes, however, are of a secondary nature.

The mode of action of lindane is still not completely understood. It is presumed that the molecules of this substance penetrate into the structure of the lipoprotein membranes of nerve cells and impair the transfer of ions at the instant of transmission of a nerve impulse. Of major significance is the space structure of the molecules. Hexachlorocyclohexane can apparently also disrupt in insects the metabolism of lipids from the group of inositol derivatives, competing with the structurally close mesoinositol. Lindane is not an exact structural analogue of mesoinositol, but the introduction of the latter into an insect's organism weakens the action of sublethal insecticide doses. The effect of lindane manifests itself in the accumulation of unusually large amounts of cholesterol in the tissues of the poisoned insect. The insecticide can therefore be presumed to act on the lipoprotein-sterine complexes of the cell structures.

The toxicity of lindane varies depending on the ambient temperature. Its contact and stomach effect grows with a decreasing air temperature, while its fumigation effect increases with a growing temperature, but here the duration of the effect diminishes.

Lindane undergoes a variety of transformations in an insect's organism (see Fig. 3).

The products of these transformations, and sometimes the unchanged insecticide too, are excreted through the Malphigian tubes.

The perennial use of lindane leads to the appearance of group acquired resistance of insects. Insects that resist lindane also have a high resistance to the other organochlorine compounds. At present, lindane-resistant races of houseflies, cockroaches, some species of weevils (alfalfa, beet), the Colorado beetle and of other harmful insects have been discovered.

Side Effects. Lindane is a very strong insecticide, therefore when it is used to treat agricultural fields and forests, a considerable eradication of beneficial insects is noted. Trichogrammatidae, carabids, and predatory mites are quite sensitive to it. It is very toxic to bees and bumble-bees.

Lindane is toxic to fish and to the organisms they feed on. In addition, it greatly changes the organoleptic properties of water.

Action on Warm-Blooded Animals and Humans. Hexachlorocyclohexane is a poison with polytropic action, but it affects first of all the central and vegetative nervous system of humans and warm-blooded animals. The liver and kidneys are also greatly affected. Lindane is the most toxic (LD_{50} for rats is 125 mg/kg of live mass), whereas technical hexachlorocyclohexane, which is a mixture of isomers, is moderately toxic (LD_{50} for rats is 600 mg/kg).

All the isomers of hexachlorocyclohexane have pronounced cumulative properties. Their ingestion into an animal's organism is attended by material and functional cumulation, which is the cause of chronic poisonings.

It must be noted that the alpha and beta isomers have a higher chronic toxicity than lindane, the gamma isomer of hexachlorocyclohexane.

The no-effect dietary level (threshold dose) for rats in a chronic test was 10 mg/kg for the alpha and beta isomers, 50 for lindane, and 800 mg/kg for the delta isomer.

Hexachlorocyclohexane can penetrate into an organism orally, via the respiratory tracts, and skin (especially oil solutions). Penetration of this toxicant or its dust through the respiratory tracts is the most dangerous. A person in this case becomes poisoned very rapidly even at a concentration of 25-60 mg/m^3. When the toxicant gets onto the skin, in addition to general poisoning it may cause eczemas and dermatitus.

When it is ingested into the organism of a warm-blooded animal, hexachlorocyclohexane rapidly passes into the blood and is distributed over the organism. Already after three hours, it is detected in the brain, liver, and muscular tissues, and easily penetrates through the placenta into an embryon. Distribution terminates in 24 hours after a single ingestion, and 75% of the entire amount of lindane is detected in the fatty tissues, muscles, and skin.

Although the decomposition and excretion of HCH begin immediately after its ingestion, the insecticide remains in an organism for about two weeks. Accumulating in the fatty tissues of livestock when they systematically feed on contaminated fodder, it imparts an unpleasant taste and odour to their fat and meat.

Hexachlorocyclohexane decomposes mainly in the liver, and it is excreted through the kidneys and the gastro-intestinal tract in the form of thiophenols, phenols, and conjugates with glucuronic and sulphuric acids. Only 1-4% of the total amount of the substance is excreted in the form of the gamma isomer with the urine and feces. Unchanged lindane also passes into the milk of nursing women and lactating mammals, which creates a danger to the young generation.

Metabolism in Organisms. Notwithstanding the high persistence of HCH in biological media, it metabolizes quite rapidly in a living organism to non-toxic water-soluble substances. The first step in the metabolism of hexachlorocyclohexane is the formation in all cases of pentachlorocyclohexene as a primary product of a dehydrochlorination reaction (see Fig. 3).

In the soil, in addition, microorganisms participate in the isomerization of the gamma isomer to the alpha isomer of HCH with the formation of specific products: alpha pentachlorocyclohexene, alpha tetrachlorocyclohexadiene, penta- and tetrachlorobenzenes.

The further decomposition of pentachlorocyclohexene proceeds in different organisms in various ways, but in all cases phenols and thiophenols have been found as the main products. They are easily excreted from the organisms of animals and insects, or are included in the general process of metabolism of plants.

Characteristic of insects is the process of enzyme dechlorination proceeding with the participation of glutathione and ensuring subsequently the stepwise dechlorination of the metabolism products to dichlorophenols or dichlorothiophenols. In addition to water-soluble substances of an unknown structure, 1,2,4,5-tetrachlorobenzene, 1,2,4-trichlorobenzene and 4-chlorobenzene were also identified as metabolites.

In animals' organisms, lindane decomposes by the consecutive formation of pentachlorocyclohexene and tetrachlorocyclohexadiene-3,5. The stepwise dehydrochlorination is catalyzed by glutathione.

The second direction via tetrachlorocyclohexadiene-3,5 and 1, 2, 4-trichlorobenzene requires the expenditure of energy for the direct oxidation of the ring and leads to the formation of chlorophenols soluble in water and excreted together with the urine.

The metabolism of hexachlorocyclohexane in plants has been studied only slightly; only two metabolites are known—pentachlorocyclohexene and 1,2,4-trichlorobenzene.

The process of their excretion from plants is unknown; it is presumed that a plant can use the metabolites, including them in the general vital processes.

Use of Hexachlorocyclohexane. Lindane is highly toxic to most harmful insects. Among the latter are *Orthoptera*, including locusts; *Diptera*, *Lepidoptera*, *Coleoptera* and the larvae of these species, especially the younger ones.

At the same time, phytophagous mites and scale insects are sufficiently resistant, therefore after the prolonged use of HCH the population of these pests increases on these plantations because of the reduction in the number of their natural enemies.

Lindane is widely used for the fumigation of storage premises before they are filled. Formulations of HCH are among the main means for controlling soil-dwelling insects and cutworms. Their use is

restricted, however, because of their unfavourable toxicological properties and the change in the taste and odour of food products after treatment of the plants or soil.

At present, formulations of HCH are used in agriculture that are prepared on the basis of the 90% technical gamma isomer of the compound and on the basis of technical hexachlorocyclohexane with a content of 12% of the gamma isomer (Table 12).

Empty storage premises are disinsected by using "Gamma" smoke pots containing 60% of the technical gamma isomer, 20% of potassium chlorate, 12% of ammonium chloride, and 8% of urotropin. In a dose of 0.5-1 g of the formulation per m^3, it virtually completely exterminates the pests (weevils, flour beetles, grain moths, and meal beetles) of the stored products. The odour of the pesticide vanishes from the premises already in three days. In this connection, "Gamma" smoke pots may be used to treat empty storage premises not later than seven days before they are filled.

To prevent poisoning by HCH residues, restrictions have been introduced in the use of this insecticide, and the tolerance level of its residues in products has been established. The tolerance level of technical HCH and lindane in milk, meat, butter, and eggs is 0.005, and in all other food products is 0.5 mg per kg of product.

The tolerance level of residues of this pesticide in food for lactating animals and egg-laying poultry is 0.05, and in concentrated food and coarse fodder for livestock and poultry being fattened, 0.2 mg/kg.

HCH formulations may be used to treat non-fruit-bearing orchards with no restrictions, and fruit-bearing ones up to blossoming, provided that fodder, vegetable and berry crops are absent in the inter-row spacings. Only the seedlings of cabbage and other vegetables may be treated in sheltered soil and during 20 days after planting in the open. Cereal and industrial crops may be treated over their seedlings, alfalfa at the beginning of its growth, cotton up to opening of the bolls provided that the leaves and stems are not fed to cattle. Forests and forest belts may be treated only if there are no pastures and haymaking within their limits.

It is prohibited to feed cattle with grass growing in the inter-row spacings of treated orchards. The haulm of sugar beets and potatoes may be fed to cattle not earlier than in 75 days after treatment. After the incorporation of HCH into the soil, the sowing of root vegetables is possible only after four years.

Sections treated with HCH may be reentered only after four days have elapsed.

Cultivation of the soil, and also work in hot weather and on poorly ventilated plantings are allowed only in two weeks after treatment.

Table 12. Use of Formulations of HCH

Formulation	Concentration of working solution, % of formulation	Rate of use, kg/ha		Crop, object treated	Pests	Features of use	Harvest time, days (waiting time)
		formulation	active ingredient				
Gamma isomer of HCH, 90% technical	—	0.2-0.4 kg per 100 kg	0.2-0.4 kg per 100 kg	Grain, leguminous, industrial, vegetable and melon crops, corn	Wire worms, false wireworms, garden flea hoppers	Preplanting treatment of seeds	
	0.7	0.1-0.2	0.1-0.2	Forest belts and stands	A variety of leaf pests	Aerosol treatment with 0.7% oil solution, rate of use 15-25 litre/ha	
Gamma isomer of HCH, 4% granulated, fine-grain	—	50	2.0	Cotton	Cutworms	Introduction of granules on soil surface when planting or after emergence of shoots	
Gamma isomer of HCH, 2% granulated, fine-grain		40	1.6	Oil-bearing poppy	Ditto	Into rows over shoots	
				Alfalfa	Pea weevils, alfalfa weevils	Scattering of granules in early spring at the beginning of growth	30
		50	1.0	Sugar beets	Turnip moths	Incorporation into soil when planting or upon emergence of shoots (Kirghiz SSR)	
Gamma isomer of HCH, 2% granulated,		60-70	1.2-1.4	Oil-bearing poppy	Shoot pests	Application over shoots	
				Wheat, barley, and corn	Wireworms, false wireworms	Incorporation into soil together with sow-	

coarse-grain						ing in rows	
		50	1.0	Fruit crop nurseries	Larvae of May beetles and other soil pests	Incorporation into soil when growing sets	
Gamma isomer of HCH, 50% wettable powder	0.04-0.08	0.6-0.8	0.3-0.4	Areas populated by locusts	Asian, Marocco, Italian locusts, field crickets	Spraying with establishing of quarantine conditions for cattle grazing and hay-mowing	30
	0.08	0.8-1.5	0.4-0.8	Grapevines	Vine lice	Spraying of parent seedling (non-fruit-bearing) vines. First treatment between beginning of budding and appearance of second leaf. Second — upon appearance of 10-12th leaf on shoot	30
		0.6-0.8	0.3-0.4	Potatoes	Colorado beetles	Spraying in vegetation period	75
		0.8	0.4	Sugar beets	Common and gray weevils		
		0.6-1	0.3-0.5	Cotton	Turnip moths		
	0.2-0.25	0.8-1.5	0.4-0.7	Apple tree	European apple sawflies	Spraying before blossoming	60
		0.6-0.8	0.3-0.4	Mustard, alfalfa	Shoot pests	Spraying over shoots	
		0.6-0.8	0.3-0.4	Winter wheat	Cereal leaf beetles		
	0.1	0.3-0.5	0.2-0.3	Peas	Pea beetles	Treatment during vegetation period	

Table 12 (*continued*)

Formulation	Concentration of working solution, % of formulation	Rate of use, kg/ha		Crop, object treated	Pests	Features of use	Harvest time, days (waiting time)
		formulation	active ingredient				
Gamma isomer of HCH 16% mineral oil emulsion	0.5	8-9 litres of suspension per 1000 trimmed sets, 10-13 litres per 1000 sets, 5-6 litres per 1000 slips		Grapevine planting stock	Vine lice	Treatment of planting stock and vine slips against root vine louse according to instructions of USSR Min. of Agriculture (1976)	
				Areas infested by locusts	Asian, Marocco, Italian locusts, field crickets	Spraying with establishing of quarantine conditions for cattle grazing and hay-mowing	30
	0.1-0.3	2.5	0.4	Sugar beets	Mangold flea and leaf beetles, common and gray beet weevils	Treatment of shoots	
				Cotton, corn, wheat, barley	Turnip moths, beet webworms, gamma moths, frit and Hessian flies	Grain crops before stem extension stage	
				Potatoes	Colorado beetles	Spraying of plants to kill second generation	

				Grapevine	Vine lice	Treatment before blossoming	
	0.6	1-2	0.1-0.3	Non-fruit-bearing orchards	Gypsy, lackey, and brown-tail moths, pierid butterflies, apple and leaf roller moths, sawflies, leaf hoppers	Allowed during vegetation period	
				Parent seedling grapevines	Vine lice		
		2-2.5 g/m²	0.3-0.4 g/m²	Storage premises	Weevils, flour and meal beetles, grain moths	Treatment of empty premises	10 days before filling
	1.5	8-9 litres of suspension per 1000 trimmed sets, 10-12 litres per 1000 untrimmed sets, 5-6 litres per 1000 slips		Grapevine planting stock	Vine lice	Treatment according to temporary instructions on moist disinfection of grape planting stock with HCH formulations, USSR Min. of Agriculture (1976)	
Formulations Based on Unconcentrated Hexachlorocyclohexane							
HCH technical (12% of gamma isomer)				Non-fruit-bearing orchards	Silkworm and brown-tail moths, pierid butterflies, leaf roller moths and other leaf pests	Aerosol treatment at a rate of 15-20 litre/ha	
	4	0.6-1.0	0.07-0.1	Forest stands, grain, sunflower	Shoot pests	Aerosol treatment of shoots, 15-25 litre/ha	

Table 12 (*concluded*)

Formulation	Concentration of working solution, % of formulation	Rate of use, kg/ha		Crop, object treated	Pests	Features of use	Harvest time, days (waiting time)
		formulation	active ingredient				
HCH, 12% dust		10-20 kg/tonne	0.12-0.24 kg/tonne	Seeds of agricultural crops	Wireworms, false wireworms, garden flea hoppers	Powdering of seeds	
				Areas infested by locusts	Asian, Marocco, Italian locusts, field crickets	Dusting with establishing of quarantine conditions for cattle grazing and hay-mowing	30
		10-25	0.12-0.3	All crops except root vegetables for food and fodder	Soil-dwelling pests	Incorporation into soil when or before planting	
				Non-fruit-bearing orchards, forest, forest belts	Leaf pests	Dusting during the season	
		20-25	0.24-0.3	Grapevines	Vine lice	Dusting before blossoming	
				Tobacco	Shoot pests	Dusting not later than in 30 days af-	

						ter planting in field	
				Cotton	Boll and beet armyworms	Dusting during the season	Up to boll opening
		15-20	0.18-0.3	Sunflower, mustard, flax, hemp	Shoot pests	Dusting of the shoots	
				Sugar beets	Common and gray beet weevils		
		15-20	0.18-0.24	Alfalfa	Pea and alfalfa weevils	Dusting at the beginning of growth at a plant height up to 12 cm	
		10-15	0.12-0.18	Cabbage and other vegetables	Blue fleas, cabbage maggots, cabbage butterflies and moths	Treatment only of seedlings and not later than in 20 days after planting in field	
		10-20	0.12-0.24	Grain, corn	Beet webworms, turnip and gamma moths	Dusting of shoots	
HCH, 25% powder on phosphorite flour		6-8	1.5-2.0	All crops except root vegetables for food and fodder	Soil-dwelling pests	Incorporation into soil before belt planting or drill seeding	

1. Polychloroterpenes

Chlorinated terpenes, like most organochlorine compounds, are quite stable in field conditions and may be retained in the soil up to 10 years. They may migrate from the soil into water basins, and also penetrate into the vegetating parts of plants and accumulate in them. These toxicants do not burn plants in the recommended concentrations.

Polychloroterpenes are stomach and contact insecticides affecting insects' nervous systems; they are very toxic to weevils, garden flea hoppers, and Colorado beetles, but have a comparatively low toxicity to bees. They also partly have acaricidal properties. Their temperature coefficient is positive, which explains why they are effective only at a temperature above 18 °C.

They are highly and moderately toxic to humans and warm-blooded animals, with a slight cumulation, but with a pronounced dermal and very acute inhalation effect. Indications of poisoning appear in humans at a concentration of polychloroterpene vapours in air of 4 mg/m^3.

Among the compounds of this group, toxaphene and polychloropinene have found the greatest favour.

Toxaphene (Polychlorocamphene, Camphechlor)

This insecticide is a mixture of chlorinated terpenes of the general formula $C_{10}H_{10}Cl_8$ prepared by the chlorination of camphene. The technical product is a wax-like substance of a light or dark brown colour with a chlorine content of 67-69%. It is virtually insoluble in water (about 3 mg/litre at room temperature), but dissolves well in most organic solvents. The volatility of polychlorocamphene is not high. When heated, it decomposes with the liberation of hydrogen chloride.

This process is intensified under the action of alkalies, iron salts, or ultraviolet rays, and may occur in natural conditions.

The toxicant is quite persistent on treated surfaces, in water, and in the soil. Residues of toxaphene are found on sugar beet plants even in 50 days after treatment at a rate of 1.5 kg/ha.

At a temperature of 18-20 °C and natural lighting, the insecticide is retained in water up to 60 days. In coarse soils, polychlorocamphene persists up to three years, and in soils with a high absorptivity, up to 10 years.

The residues of the insecticide in the soil are one of the main sources of contaminating agricultural products with this substance. It is absorbed in a considerable amount from the soil by perennial grass and by root vegetables. This is why a tolerance level of this insecticide in the soil has been established (not over 0.5 mg/kg).

In its recommended concentrations, toxaphene does not cause the burning of plants, which together with its low toxicity to bees allows it to be used for the treatment of plants during their blossoming period.

Toxaphene relates to highly toxic substances (LD_{50} for rats is 45-400 mg/kg) with acute dermal and a weakly expressed cumulative effect. It persists for a long time in the organisms of humans and animals—at a single ingestion of a dose at the level of LD_{50}, up to 14 days; it may be secreted with a nursing mother's milk. When it is ingested into the organism of a warm-blooded animal, toxaphene affects first of all the nervous system and liver. The penetration of this insecticide through the respiratory tracts is especially dangerous—poisoning occurs at a content of 4 mg of the substance in 1 m^3 of air.

When ingested into a human organism orally, a dose of 10 mg/kg and even less may cause intoxication, while 60 mg/kg may be lethal. Cases are known of poisoning when greens were eaten containing from 3.3 to 13.3 mg of toxaphene per kg.

The feeding of fodder contaminated with this insecticide to cattle leads to its accumulation in the animals' fat. Residues of toxaphene are detected in the fatty tissues during eight weeks after stopping the use of contaminated fodder.

In agriculture, a 50% emulsifiable concentrate of toxaphene is used containing 50% of the technical product, 30% of non-phytotoxic mineral oil, and 15% of OP-7. It is applied in the form of a 0.4-0.5% emulsion. It is highly effective in controlling pests of sugar beets (common and gray beet weevils, mangold flea beetles), Colorado beetles on potatoes, pea weevils on peas and leguminous grasses, and the pests of rape and mustard. Leguminous grasses may be treated during their blossoming stage to control seed-eating insects. The rate of use of this insecticide is 1.6-3 kg (0.8-1.5 kg a.i.) per hectare.

To reduce the danger of toxaphene getting into fodder and food products, the shoots of sugar beets, rape, mustard, and potatoes may be treated only to control the first two generations of the Colorado beetle. Grass, the haulm of potato, pea, sugar beet, rape, and mustard plants may be used as fodder and peas may be ground into flour not earlier than in 75 days after treatment of the crops with the insecticide. It is prohibited to use green peas for canning or other purposes. The tolerance level of toxaphene in potatoes and sugar beets is 0.1 mg/kg. No residues are tolerated in the food for lactating animals and egg-bearing poultry; these residues must not exceed 0.25 mg/kg in the food for animals and poultry being fattened.

The maximum tolerated concentration in the air of the working zone is 0.5 mg/m^3. Workers are forbidden to reenter treated areas during four days after the application of toxaphene.

During the following two weeks, all work on these fields may be performed only with the use of individual means of protection.

Polychloropinene

The product of chlorination of bornyl chloride prepared from the pinene fraction of turpentine contains 64-67% chlorine. Its general formula is $C_{10}H_{10}Cl_8$. The technical product contains terpenes with various degrees of chlorination and other related organic compounds.

Technical polychloropinene is a viscous colourless substance whose consistence reminds one of honey. It is virtually insoluble in water, and well soluble in organic solvents. It is similar to toxaphene in its chemical properties. It may persist in the soil over a year, in water and on plants up to 60 days. From contaminated soil, it enters plants, remaining in them for a long period. The tolerance level of polychloropinene in soil is 0.5 mg/kg.

Polychloropinene is more phytotoxic than toxaphene. For this reason, the burning of plants is possible in treatments, especially when solutions in diesel fuel are used. It is more toxic to bees and entomophags. It is prohibited to use polychloropinene during the blossoming of plants.

Polychloropinene is a contact and stomach insecticide. It is similar in its spectrum of action to toxaphene, but is characterized by repellent properties.

It is moderately toxic to man and animals (LD_{50} is 240-500 mg/kg for mice), but has a pronounced cumulative and dermal toxicity, and a high inhalation toxicity.

Formulations based on polychloropinene, owing to their high effectiveness and cheapness, are used to control the pests of potatoes, sugar beets and leguminous crops. They are good killers of mangold flea beetles, common beet weevils (they act weakly on gray beet weevils), young larvae and young adults of the Colorado beetle, and also of pea weevils and other pests of leguminus crop shoots. To increase the toxicity to sugar beet pests, a mixture of insecticides (polychloropinene plus a concentrate of a lindane emulsion) in the ratio of 1 : 1 may be used.

The chemical industry manufactures a 65% emulsifiable concentrate containing 65% of technical polychloropinene, 20% of non-phytotoxic mineral oil, and 15% of OP-7. It is used for spraying in controlling the pests of potatoes, sugar beets, and leguminous plants in a concentration of 0.7-1% with a rate of use of 1.6-3 kg or 1.0-2.0 kg a.i. per hectare.

Owing to the high persistence of polychloropinene, restrictions have been introduced for its use in agriculture. Workers may reenter treated fields without means of protection not earlier than in two weeks after chemical treatment. This insecticide may be used to treat only shoots of sugar beets, leguminous plants, and potatoes. The haulm of sugar beet, potato, and pea plants may be used for fodder and silage and peas may be ground into flour only in 75 days after

treatment. It is prohibited to use the green peas for any purposes. No residues of polychloropinene are allowed in food products and foods for lactating animals and egg-bearing poultry. Succulent fodder for animals and poultry being fattened may contain 0.5 mg/kg, and coarse fodder—1.0 mg/kg.

2. Polychlorocyclodienes

This group includes highly active insecticides prepared by the Diels-Alder reaction of condensation of cyclopentadiene with unsaturated compounds such as quinone.

Polychlorocyclodienes are contact and stomach insecticides; some of them have systemic and fumigation action. Upon ingestion into an insect's organism, they act first of all on the nervous system. In addition, cyclodiene compounds can inhibit the activity of respiratory enzymes, particularly of dehydrogenase succinate. Poisoning by these substances is attended by a sharp drop in the intensity of respiration and disruption of the processes of oxidizing phosphorylation in insects.

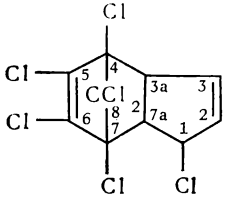
Polychlorocyclodienes often stimulate the growth of the plants being protected.

Most cyclodiene compounds are strong and highly toxic poisons to humans with sharply pronounced cumulative properties.

A feature of these insecticides is their ability to cause general poisoning of an organism when absorbed through the skin. In view of their high persistence in various media and their unfavourable toxicological properties, the use of these compounds is greatly restricted. Heptachlor, endosulfan, dilor, and despirol are allowed to be used in agriculture in the USSR.

Heptachlor

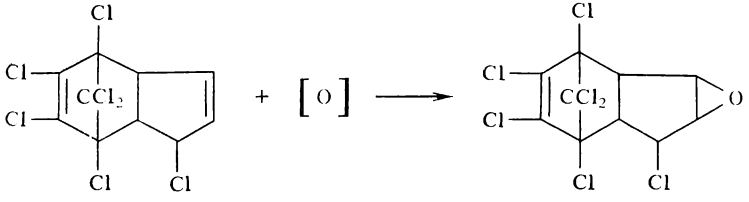
The active ingredient is 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene:



Pure heptachlor is a white crystalline substance with a mild camphor odour melting at 95-96 °C. It has a comparatively high volatility and in a closed space can create a concentration close to the

toxic one. It is virtually insoluble in water, moderately soluble in ethyl alcohol, and is well soluble in aromatic hydrocarbons and halogen derivatives of hydrocarbons.

The substance is chemically stable, decomposes only slightly in water and under the action of alkalies. Oxidizing agents lead to the formation of the epoxide of heptachlor, which is more toxic to all kinds of organisms and is no less stable than heptachlor:



The reaction may occur in living organisms and in the soil with the participation of various enzyme systems.

The high chemical stability of heptachlor and its epoxide underlies the prolonged persistence of these compounds in the soil and on the surface of plants. In the soil, heptachlor decomposes under the action of microorganisms to form both more toxic and less toxic compounds (Fig. 4).

Chlordene and heptachlor epoxide are highly toxic to warm-blooded animals, while chlordene 1-exohydroxide has a low toxicity (LD_{50} for rats is 2400-4600 mg/kg).

The processes of decomposition of heptachlor proceed relatively slowly, however, and for this reason it persists in the soil from two to five years. In plants, heptachlor is detected even in 60 days after treatment.

The toxicant penetrates readily from the soil through the roots of plants into their green organs and displays systemic action. After the treatment of seeds with heptachlor, stimulation of the growth of plants is noted. When used to spray shoots, heptachlor does not cause burning and does not adversely affect their growth.

Heptachlor is a contact and stomach insecticide. When incorporated into the soil together with seeds, it also exhibits systemic and local fumigational action. The shoots of plants are protected from attack by harmful insects during two weeks and more.

Like all organochlorine compounds, heptachlor affects the nervous system first of all. In insects' organisms, it is oxidized to the epoxide, which evidently inhibits their vital systems.

Heptachlor is highly toxic to various beetles and their larvae, including soil-dwelling ones, to cutworms, and other pests of agricultural plant shoots.

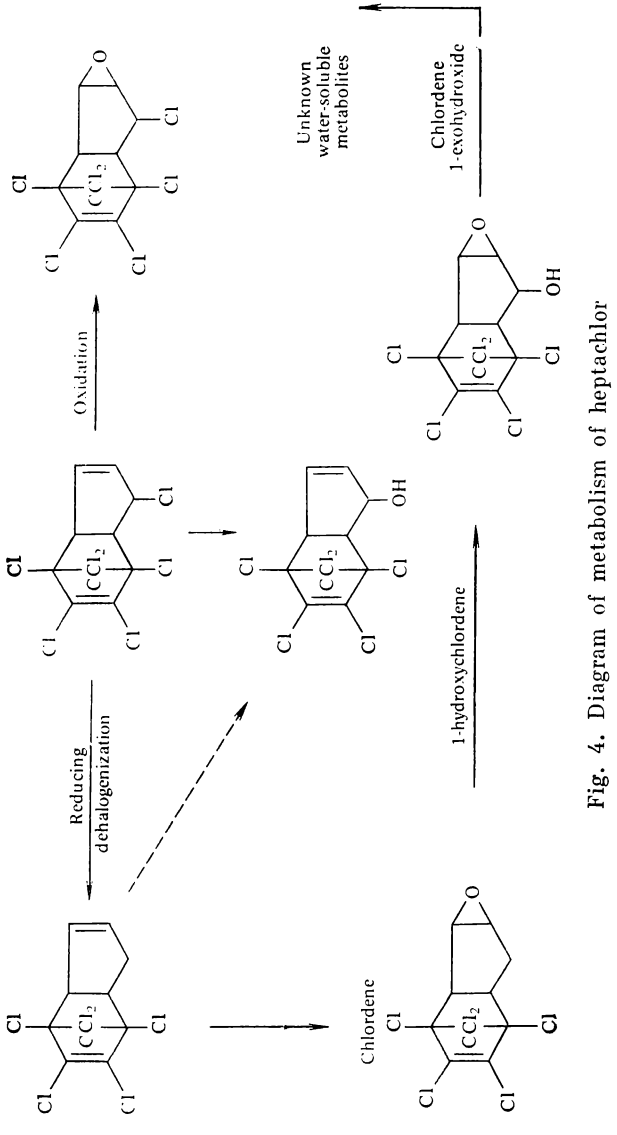


Fig. 4. Diagram of metabolism of heptachlor

The insecticide is highly toxic to humans and warm-blooded animals (LD_{50} for rats is 90 mg/kg) and has sharply pronounced cumulative and inhalation toxicity. When it gets onto the skin and mucous membranes, it causes their inflammation and dermatitis.

Indications of poisoning of humans are noted already at a concentration of thousandths of a milligram of heptachlor in 1 m^3 of air. In animals' organisms, heptachlor is deposited in the fatty tissues in the form of the epoxide or in an unchanged form, and may then be secreted with the milk of lactating animals and cause poisoning of young individuals. This is why residues of heptachlor in food products and fodder are not tolerated.

The maximum tolerated concentration in the air of the working zone is 0.01 mg/m^3.

A 22% emulsifiable concentrate of heptachlor is marketed for controlling agricultural pests. The use of this insecticide is greatly restricted because of its high toxicity and persistence.

It is of great significance as a means for treating seeds against wireworms, false wireworms, larvae of cockchafers, earth crabs, grass flies, cereal leaf beetles, and cutworms. Heptachlor is persistent in soils with an alkaline reaction of the medium, is cheap, and has systemic action. This explains its use as an addition to seed disinfectants in industrial production, and for the preplanting treatment of sugar beet and corn seeds.

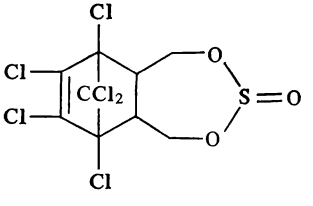
The rate of use of the insecticide for treating these seeds is 5-7 kg and 2-6 kg/tonne, respectively.

The shoots of cultural plants remain toxic to insects for up to 30 days.

By the time of harvesting, no residues of the insecticide are found in the plants.

Endosulfan (Thiodan, Benzoepin)

The active ingredient is 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide:



Two stereoisomers of the active ingredient are known: alpha-endosulfan [endosulfan (I)] melting at 108-110 °C and beta-endosulfan [endosulfan (II)]—208-210 °C. They differ insignificantly in their

physicochemical and toxic properties. They are white crystalline substances insoluble in water, well soluble in organic solvents, virtually non-volatile, and quite stable in light. The ratio of these isomers in the technical product is 4:1.

Endosulfan is chemically less stable than the other polychlorocyclodienes. In an alkaline and neutral medium, it readily hydrolyzes to endosulfan alcohol having a low toxicity to humans and animals. Oxidizing agents transform it into endosulfan sulphate whose toxicity is virtually the same as that of endosulfan (I). These processes also occur in natural conditions on the surface of plants, in the water of various basins, and in the soil. When it gets into the soil, the insecticide persists for a year and more.

Endosulfan does not burn plants in the recommended concentrations. Conversely, reports have been received on its stimulating action. It does not penetrate into plants through their leaves or through their roots, therefore residues of the insecticide do not accumulate in the tissues of plants even with considerable contamination of the soil with them. They vanish from the surface of plants because of the action of environmental factors, which may take considerable time. Metabolism of the insecticide, as in a plant, consists in hydrolysis and oxidation with the formation of endosulfan sulphate and endosulfan alcohol (Fig. 5).

Endosulfan is a contact and stomach insecticide and acaricide having a high toxicity to beetles, *Lepidoptera* and their larvae, and also to mites. Its persistence in field conditions is about 15 days. A major advantage of this toxicant is its exclusive effectiveness in monitoring big bud and strawberry mites.

Upon penetrating into an insect's organism, endosulfan inhibits the functions of its nervous system, becoming oxidized in the first step of metabolism into the no less toxic endosulfan sulphate (see Fig. 5). Further transformation follows the path of the formation of water-soluble products: endosulfan ether, hydroxyendosulfan ether, and endosulfan lactone, which are excreted from the organism through the system of Malpighian tubes. A part of the active ingredient is excreted with the feces in an unchanged form.

Endosulfan has a low toxicity to bees and entomophags from the genus *Coccinellidae*, which allows it to be used in integrated control systems.

The insecticide is highly toxic to humans and warm-blooded animals both upon oral ingestion (LD_{50} for rats is 40-100 mg/kg) and in dermal application (the dermal LD_{50} for rats is 35 mg/kg). It has moderately expressed cumulative properties with a cumulation coefficient of 3.6.

Endosulfan vanishes comparatively rapidly from an organism without accumulating in the fatty tissue. Hydrolytic processes in an animal's organism result in the formation of water-soluble meta-

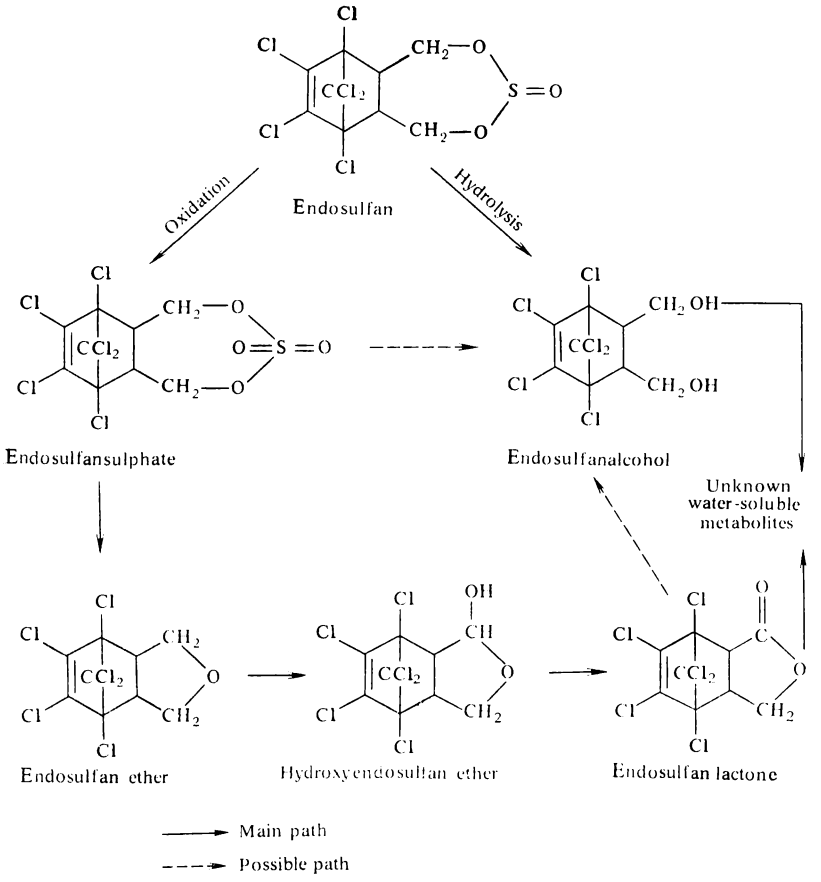


Fig. 5. Diagram of metabolism of endosulfan

bolites (see Fig. 5) that are excreted with the urine. Part of the untransformed insecticide is traced in the feces. An insignificant secretion of endosulfan with the milk of mammals is also noted.

Endosulfan is relatively harmless to wild animals and birds. No cases of perishing of animals and insectivorous birds after its use have been registered. When it gets into water basins, however, it may kill fish.

In agriculture, a 50% wettable powder of endosulfan is used. In a concentration of 0.3-0.4%, it is good against larvae and adults of big bud and strawberry mites. Currant bushes are treated twice: the first spraying is before blossoming, and the second 15 days later,

which corresponds to the beginning of migration and the mass migration of the mites. The larvae of black-currant midges and aphids are exterminated simultaneously. The rate of use of the insecticide is 3-6 kg (1.5-3 kg a.i.) per hectare.

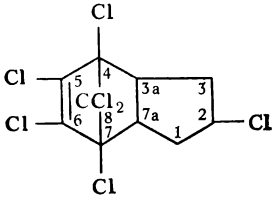
On cotton fields, the pilot application of endosulfan to control bollworms and beet armyworms has been allowed at a rate of 2.0-2.5 kg (1.0-1.25 kg a.i.) per hectare. To diminish the contact with the toxicant of persons working on the fields, the treatment should be performed after chopping of the cotton and terminated before the bolls open. Upon the intensive development of the spider mite, endosulfan may be combined with specific acaricides—dicofol, dinobuton, milbex, etc.

The insecticide is recommended for controlling alfalfa and clover seed pests at the same rate of use. It is prohibited to use treated plants as fodder for livestock.

Owing to endosulfan's high toxicity and persistence, it is permitted to use it only on breeding plantations of strawberries and black currant bushes with prohibiting of the use of the berries for food. Residues of the insecticide in food products are not tolerated. Persons using endosulfan must take special care to protect their skin from the substance getting onto it.

Dilor (Dihydroheptachlor)

The active ingredient is 2-exo, 4,5,6,7,8,8-heptachloro-3,4,7,7-tetrahydro-4,7-methanoindane:



The technical product is a mixture of three stereoisomers of dilor: alpha, beta, and gamma, of which the alpha and beta isomers have the highest insecticidal activity and contain at least 98% of the active ingredient. The latter is a gray compound with a weak odour melting at 128 °C. It is virtually insoluble in water and sparsely soluble in organic solvents (in xylene—about 10%).

In its chemical properties, it is identical to the other polychlorocyclodienes, having a somewhat lower persistence.

In its recommended doses, dilor does not burn plants and has no negative effect on the quality of the products. Its residues are traced in plants during a month after treatment.

Dilor is a contact and stomach insecticide. It can penetrate deeply into plants. In its toxicity to insects, it is not inferior to chlorinated terpenes; it is highly toxic to beetles and *Lepidoptera*, and also to their larvae. The protective action continues for 12 to 15 days. When the temperature lowers, the effectiveness of the toxicant diminishes.

Dilor has a low toxicity to humans and animals (LD_{50} for laboratory animals is 2000-9000 mg/kg), its dermal toxicity is expressed only slightly, and it has moderately expressed cumulative properties. It has a toxic effect on the liver. When it gets into animals' organisms, it metabolizes relatively rapidly with the substitution of the chlorine in the 2-exo-position by a hydroxyl group and the following formation of the water-soluble and only slightly toxic trans-2,3-dioxy-4,5,6,7,8,8-hexachloro-4,7-endomethylene-3a,4,7,7a-tetrahydroindane.

An 80% wettable powder of dilor is recommended for controlling the Colorado beetle on potatoes at a rate of 0.3-0.6 kg (0.2-0.5 kg a.i.) per hectare and common and gray beet weevils on sugar beets at a rate of 1.5-2 kg (1.2-1.6 kg a.i.) per hectare. Potatoes are sprayed beginning from the moment of the mass birth of larvae of the Colorado beetle, the rate of use of the insecticide being regulated depending on the stage of development of the pest. Sugar beets are treated beginning from the two-leaf stage, with repetition of the treatment every 7-10 days.

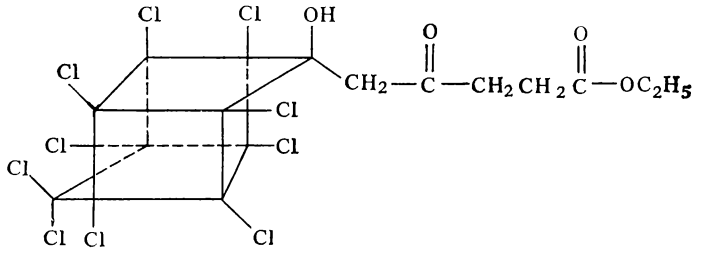
For controlling vine lice on parent vines of seedling species of grapevines, the formulation is used in a concentration of 0.5% of the insecticide at a rate of 500 litres (4 kg a.i.) per hectare.

The pilot use of dilor for treating tomatoes and eggplants to monitor the Colorado beetle has been permitted at a rate of 0.6-0.8 kg (0.5-0.6 kg a.i.) per hectare, to control bollworms on cotton fields at a rate of 3-4 kg (2.4-3.2 kg a.i.) per hectare, and to control phytonomus in alfalfa plants at a rate of 3-5 kg (2.4-4 kg a.i.) per hectare.

When spraying plants with dilor, the suspension must be thoroughly applied to them. The harvest time for potatoes is 20 days, for sugar beets, eggplants, and cotton is 30, and for alfalfa is 45 days. The tolerance level of dilor in vegetables, potatoes, and sugar beets is 0.2 mg/kg.

Despirol (Kelevan)

The active ingredient is ethyl-1,1a,3,3a,4,5,5a,6-decachloro-octahydro-2-hydroxy-1, 3, 4-metheno-1H-cyclobuta(c, d)pentalene-2-laevulinat:



Pure despirol is a brown powder melting at 91 °C. It is virtually insoluble in water, and is soluble in acetone, alcohol, benzene, toluene, and chloroform.

It is slowly hydrolyzed by water, but with an increase in the pH and under the action of solar radiation the process is accelerated. The toxicant hydrolyzes on treated surfaces in the course of a month.

No negative influence on the growth and development of plants has been noted.

Despirol is a stomach insecticide with a less pronounced contact toxicity and a prolonged protective action.

It is highly toxic to beetles, especially to weevils. It is virtually harmless to bees and other beneficial insects.

The insecticide is moderately toxic to humans and animals (LD_{50} for rats is 240-280 mg/kg), its dermal toxicity is weak, and it has no cumulative properties.

In the USSR, a 50% wettable powder of despirol is recommended for pilot use to control the Colorado beetle on potatoes—0.3-0.4 kg of the formulation (0.15-0.2 kg a.i.) per hectare, and on tomatoes and eggplants—0.3-0.5 kg (0.15-0.25 kg a.i.) per hectare, to control common beet weevils—1-2 kg (0.5-1 kg a.i.) per hectare, and also gray and black weevils on sugar beets—1.5-3 kg (0.75-1.5 kg a.i.) per hectare. Treatments are commenced from the moment of appearance of the pests and are repeated every 8-12 days; when the temperature of the air drops, the rate of use of the insecticide is increased without exceeding the recommended limits. The harvest time is 30 days.

3. Specific Acaricides

Up to recent times, the problem of controlling phytophagous mites was successfully coped with by means of insectoacaricides from the group of organophosphorus compounds. But it was found that after the perennial use of these substances, group resistance to organophosphorus compounds appears quite rapidly in mites. The rate of appearance of this resistance grows with an increasing number of genera-

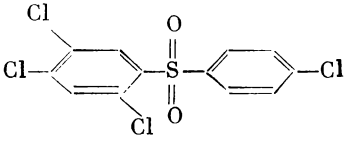
tions of the mites during a season; in a short time, the resistance may increase 100 times and more.

In this connection, the need appeared of having acaricides whose mechanism of action differs. As a result of work in this direction, many substances have appeared that have been combined according to the mode of their action into the group of specific acaricides. They include a variety of synthetic organic substances: sulphoacid derivatives and sulphones, organochlorine and azocompounds, and derivatives of carbonic and propionic acids. Most of them have no insecticidal properties. The specific acaricides kill phytophagous mites in all the stages of their development. A feature of these toxicants is their prolonged persistence. The specific acaricides are moderately or only slightly toxic to humans and animals and do not cause harmful side effects.

Tetradifon (Tedion)

Tetradifon relates to the group of sulphones. The insecticidal action of most sulphones is not great, but a number of active acaricides have been earmarked among them. Compounds of the aromatic series containing chlorine in the positions 2,4, and 5 in one aromatic ring and a fluoro, chloro, bromo, or methoxy group in the position 4′ in a second ring have the highest activity. Of these compounds, tetradifon has found the greatest favour.

The active ingredient is 2,4,4′,5-tetrachlordiphenyl sulphone (or 4-chlorophenyl 2,4,5-trichlorophenyl sulphone):



It is a white crystalline substance melting at 148-149 °C. It is insoluble in water (0.2 g/kg at 50 °C), methyl alcohol, and petroleum ether, and is well soluble in chloroforms, aromatic hydrocarbons, and ketones.

It is chemically stable, which is explained by the high strength of the S—C bonds (of the ring).

Tetradifon is stable to the action of mineral acids and alkalies even upon prolonged heating.

Owing to its high chemical stability, tetradifon persists for a long time on the surface and inside plants, protecting them from mites during 60-80 days after treatment. When applied to leaves, it penetrates into the tissues, but does not move along the plant. In the recommended concentrations, it does not burn plants and does not detract from the quality of the crop.

Tetradifon is a contact acaricide with a low initial toxicity and a prolonged protective action. It is highly toxic to summer eggs and young larvae and is only slightly toxic to adult mites and wintering eggs.

It does not virtually act on beneficial insects, which allows it to be used for controlling acarapidosis—a quarantine disease of adult bees.

Tetradifon has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 5000 mg/kg), and has no chronic nor dermal toxicity.

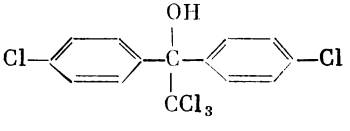
The industry markets 30% and 50% wettable powders of tetradifon. They are recommended for controlling fruit-tree and red and brown spider mites in apple orchards at a rate of 0.7-2.4 kg a.i./ha (2.4-8 kg of 30% and 1.4-4.8 kg of 50% formulation); for controlling spider mites on grapevines—0.5-1.8 kg a.i./ha (1.8-6 kg of 30% and 1.0-3.6 kg of 50% formulation); for controlling citrus red mites on citrus fruit plantations—1.8-2.7 kg a.i./ha (6-9 kg of 30% and 3.6-5.4 kg of 50% formulation); for controlling spider mites on cotton, open-ground vegetable crops, and melons—0.9-1.5 kg a.i./ha (3-5 kg of 30% and 1.8-3 kg of 50% formulation); for controlling spider mites on cucumbers in hotbeds and greenhouses—0.9-2.7 kg a.i./ha (3-9 kg of 30% and 1.8-5.4 kg of 50% formulation).

To increase the effectiveness of tetradifon, it should be used in a mixture with organophosphorus acaricides.

The last treatment of all crops with tetradifon must be not later than 20 days before harvesting; cucumbers in hotbeds and greenhouses may be treated five days before harvesting with obligatory thorough washing with water when harvesting. The tolerance level in fruit and vegetables is 0.7 mg/kg.

Dicofol (Kelthane, Chloroethanol)

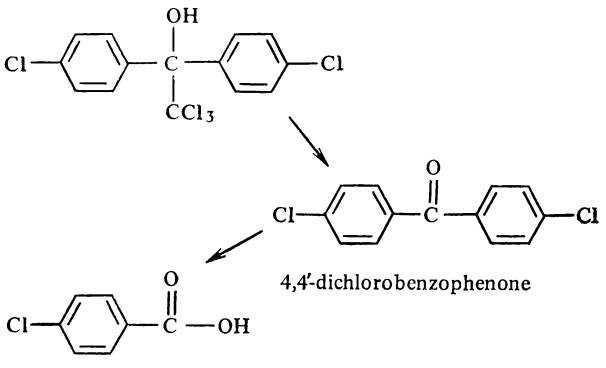
The active ingredient is 4,4′-dichloro-alpha-trichloro-methyl-benzhydrol, or 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol:



In the pure state, it is a solid melting at 78.5-79. °C, insoluble in water, but well soluble in organic solvents. Dicofol is sufficiently stable in water and in an acid medium, but under the action of alkalies it readily decomposes with the formation of non-toxic products.

It persists for up to 50 days on the surface of treated plants. In the recommended concentrations, it does not burn plants, including cultures in sheltered soil, and does not detract from the quality of the harvest of agricultural crops. Upon penetrating into plants,

dicofol decomposes into non-toxic products:



4-chlorobenzoic acid

Dicofol is a contact acaricide with a high initial toxicity to and a prolonged residual action on most species of phytophagous mites. It is a good killer of the mobile stages of mites—adults and larvae. The protective action of kelthane continues two or three weeks on cotton, 20 days in sheltered soil on cucumbers, and up to 40 days in orchards on fruit trees. The acaricidal action of the formulation manifests itself only upon the maximum contact with the pests, therefore complete covering of the plants with the working solution is desired.

Laboratory tests have shown that repeated treatments with dicofol lead to resistance to this acaricide. This is why it is recommended to use dicofol in a system of acaricide alternation both for zones where mites exhibit a high resistance to organophosphorus compounds and for regions where there is no resistance.

Dicofol is moderately toxic to humans and warm-blooded animals (LD_{50} for mice is 430 mg/kg, and for rats is 900 mg/kg), has acute dermal and acute chronic toxicity (the cumulation coefficient is 1.2), and an appreciable mutagenic action.

Two formulations are available on the market: a 20% emulsifiable concentrate and an 18.5% wettable powder. When tested in field conditions, both formulations showed the same effectiveness.

Dicofol is recommended for the protection of fruit orchards (apple, pear, plum, sour and sweet cherry trees) in a concentration of 0.2% of the formulation against fruit-tree brown and red spider mites and hawthorn mites at a rate of use of 1.6-5.0 kg (0.3-1 kg a.i.) per hectare; against spider mites on open-ground vegetable and melon crops—0.4-1 kg a.i. or 2.0-5 kg of the formulation per hectare; on cotton—0.6-1 and 3.0-5 kg/ha, respectively; on grapevines—0.3-0.8 and 1.5-4 kg/ha; on hops—0.4-1.4 and 2.0-7 kg/ha; on strawber-

ries, currants, and gooseberries—0.3-0.6 and 1.5-3 kg/ha, respectively; against citrus red and rust mites on citrus plantations at a rate of 8-10 kg of the formulation (1.6-2 kg a.i.) per hectare; and against spider mites on vegetable crops in sheltered soil—8.0-10.0 kg (1.6-2.0 kg a.i.) per hectare.

Berry (small fruit) crops are treated only in spring before blossoming, and after the crop has been gathered. When variety sensibility of agricultural crops to dicofol is revealed, it is recommended to use a wettable powder (chloroethanol) to monitor mites, regulating the rate of use within the recommended values.

The harvest time for all crops is 20 days. Cucumbers in hotbeds and greenhouses may be sprayed three or four days before harvesting, but provided that the harvested vegetables are thoroughly washed with warm water. Not more than a twofold treatment of any crops with dicofol is permitted during a season.

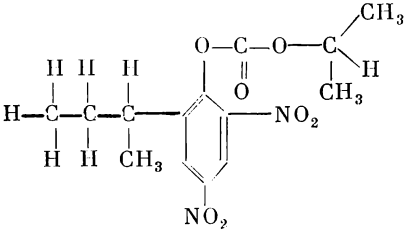
The tolerance level of dicofol in fruits and vegetables is 1 mg/kg.

Recent years have seen the use of dicofol for preparing combined pesticides with both acaricidal and fungicidal properties. Acarthane is such a substance—it contains two active ingredients, dicofol and dinocap. This allows it to be used for protecting plants against mites and powdery mildew. The pesticide has a high initial toxicity and a prolonged protecting effect. It is moderately toxic to humans and warm-blooded animals.

A 30% emulsifiable concentrate of acarthane (20% dicofol + + 10% dinocap) is recommended for controlling spider mites on cotton at a rate of 4 kg (1.2 kg a.i.) per hectare and a harvest time of 20 days.

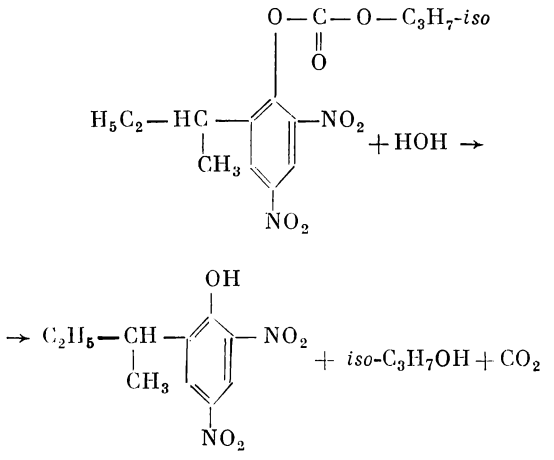
Dinobuton (Acrex, Dinofen)

The active ingredient is 2-(1-methyl-2-propyl)-4,6-dinitrophenyl isopropylcarbonate:



It is a pale yellow crystalline substance melting at 61-62 °C. It dissolves poorly in water, well in acetone and xylene, and moderately in alcohol.

Dinobuton is stable in an acid medium, but is hydrolyzed by alkalies to dinoseb—a substance with a higher toxicity to humans:



This process also takes place in living organisms, being the first step of metabolism of the substance.

Dinobuton persists on the surface of treated plants during 20-25 days, ensuring a prolonged protective effect. It penetrates into plants slowly and in a small amount (10-15% of the total amount). Inside plants, dinobuton rapidly hydrolyzes to dinoseb with its subsequent reduction to non-toxic aminophenols.

Already in 48 hours after treatment, no residues of dinobuton are detected inside plants.

The substance is not phytotoxic in the recommended concentrations, but care must be taken in treating cucumbers in the early stages of their development. When spraying cucumbers in this period, the concentration of the solution must be 0.05-0.1%.

Dinobuton is a contact acaricide with a high initial and a prolonged protective action. It is toxic to phytophagous mites in all the stages of their development. It is also an effective fungicide for controlling powdery mildew. When used to treat populations of mites resistant to organophosphorus toxicants, dinobuton lowers this resistance from three to five times during a single season. No cases of the appearance of acquired resistance to dinobuton have been registered.

Dinobuton is highly toxic to humans and warm-blooded animals (LD_{50} for rats is 119-142 mg/kg); its dermal toxicity is weak. It rapidly hydrolyzes in animals' organisms to form the highly toxic di-

noseb, which is detected in the blood in 15-30 minutes after introduction of the substance, and the carbonyl radical, which rapidly decomposes (during 24 hours) into CO_2. Dinoseb is excreted from an organism in the unchanged form with the urine and feces during 10 days after introduction, while part of the substance (40%) is reduced to aminophenols that are excreted in the form of conjugates with glucoronic acid. Dinobuton does not accumulate in animals' organisms. It has no cumulative properties.

Dinobuton is marketed in the form of a 50% wettable powder and is recommended for controlling phytophagous mites having various degrees of sensitivity to organophosphorus and organochlorine acaricides on cotton, fruit trees, vegetable, ornamental, and citrus plants.

Dinobuton is used on apple and pear trees in a concentration of 0.15-0.2% of the formulation to control fruit-tree brown and red spider mites, and hawthorn mites at a rate of 1.5-3 kg (0.8-1.5 kg a.i.) per hectare; on cucumbers in sheltered soil to control spider mites in a concentration of 0.05-0.2% of the formulation at a rate of 6-8 kg (3.0-4.0 kg a.i.) per hectare; on roses, chrysanthema, and pinks to control spider mites in a concentration of 0.2% of the formulation at a rate of 1-2.2 kg (0.5-1.1 kg a.i.) per hectare; on citrus trees to control citrus red and rust mites in a concentration of 0.1-0.2% of the formulation at a rate of 6-8 kg (3.0-4.0 kg a.i.) per hectare; and on cotton to control spider mites at a rate of the toxicant of 2 kg (1 kg a.i.) per hectare.

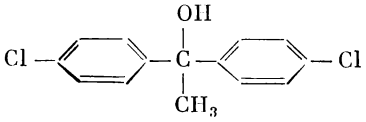
In a concentration of 0.1-0.15% of the formulation, dinobuton is recommended for controlling powdery mildew of fruit trees, berries, and flowers, and of cucumbers in sheltered soil at the rates of use indicated above.

Experience gained at the vegetable experimental station of the Timiryazev Agricultural Academy and at farms of the Moscow Region has shown that when growing cucumbers in a greenhouse, dinobuton can be successfully used to eliminate primary seats of spider mites. Subsequent treatments should be performed differentially with a view to the mite population on the plants.

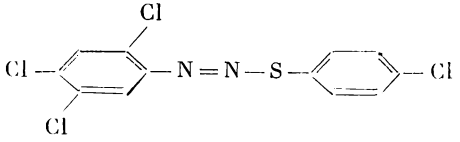
When using dinobuton on cucumbers, the last treatment must be performed not later than two days before harvesting them. The vegetables must be thoroughly washed with water. The last treatment on fruit trees, including citrus ones, flowers, and cotton may be performed at least 20 days before harvesting, and on berry plants—after harvesting and before blossoming. A 30% emulsifiable concentrate is used on cotton to control mites by spraying during the vegetation period; the rate of use is 3-3.5 kg of the toxicant per hectare. The last time of treatment is 20 days before picking the cotton. The tolerance level for cucumbers, apples, and citrus fruits is 0.05 mg/kg.

Milbex (Chlorfensulphide)

This is a combined toxicant containing two active ingredients: 1,1-bis-(4-chlorophenyl)ethanol [BCPE (dimite)]



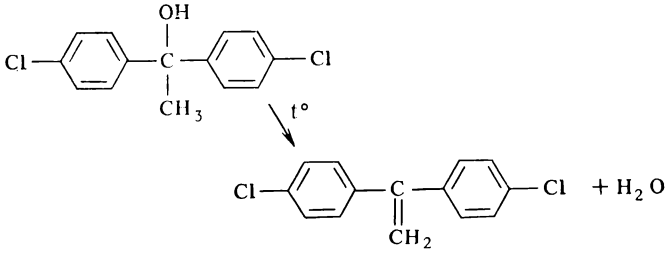
and 4-chlorophenyl-2′,4′,5′-trichlorophenyl-azosulphide (CPAS)



BCPE in the pure form is a colourless crystalline substance melting at 69.5-70 °C.

It is insoluble in water, but readily dissolves in most organic solvents. Its volatility is higher than that of dicofol, therefore BCPE is partly lost from treated surfaces because of evaporation.

BCPE has a low chemical stability, and is readily decomposed by alkalies or acids to 1,1-bis-(4-chlorophenyl)ethylene:



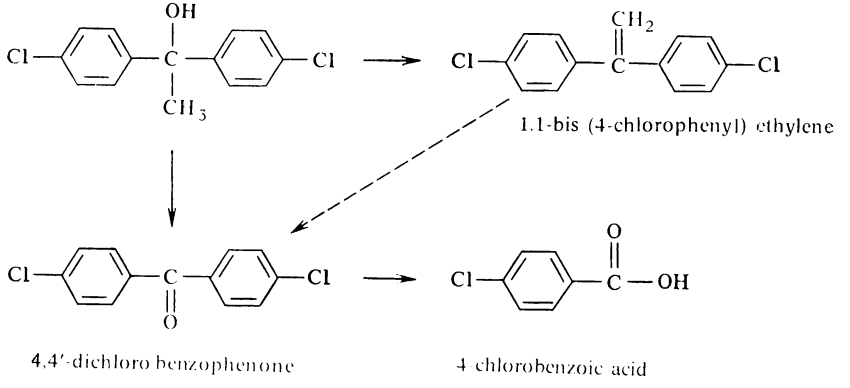
This reaction occurs when the compound is stored already at room temperature. The reaction rate grows with elevation of the temperature.

At 45 °C, 20% of the compound decomposes in 6.5 months, while at 95 °C, 61% decomposes in 24 hours. This is why in warm regions milbex may lose its toxicity and, consequently, its economical effectiveness in prolonged storage.

CPAS is a white crystalline substance melting at 123.5-124 °C. It is insoluble in water, sparsely soluble in acetone, and well soluble in alcohol, benzene, and some petroleum products.

The toxicant is stable to the action of dilute acids and alkalies, which is mainly what underlies its prolonged persistence on plants.

In the recommended concentrations, milbex does not cause the burning of fruit trees and cotton. In conditions of sheltered soil, partial burning of cucumber leaves is noted, especially at concentrations of the toxicant of 0.1% and higher. Milbex persists on plants up to 30-35 days. Its first component decomposes relatively rapidly with the formation of products having a low toxicity:



The second component is more stable; its metabolism in the tissues of plants has not been studied.

Milbex is a contact acaricide with a high initial toxicity and a prolonged protective and penetrating action. The presence in it of two compounds differing in their structure and mechanism of action expands the spectrum of action of the toxicant and prevents the rapid development of acquired resistance.

BCPE is highly toxic to larvae and adults of mites as a contact poison, and CPAS renders a sterilizing effect on females of the mites and, intoxicating the tissues of treated plants, causes born larvae to perish when they feed. The process of mites acquiring a specific resistance to milbex proceeds at a considerably slower rate than to organophosphorus and organochlorine compounds. If during three years of continuous application of dimethoate and dicofol the resistance of mites increased 100-300 and 34.7 times, respectively, their resistance to milbex increased only 2-3.8 times during the same period. The possibility of the appearance of milbex-resistant populations of mites must be taken into account, however. At the same time, milbex substantially lowers the resistance of mites to organophosphorus acaricides: during one season of treatments, their resistance drops 3-5 times. This explains the inclusion of this substance in a system of alternating acaricides for preventing the appearance of specific resistance in mites to acaricides on various crops.

Milbex does not exterminate bees and beneficial insects.

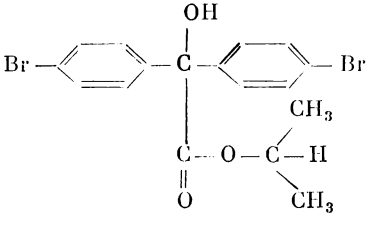
The substance has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 1200 mg/kg). It penetrates through the undamaged skin and has slight cumulative properties (at a dose of 1/20 of LD_{50}). According to the data of an Uzbek Research Institute, milbex in doses of 1/20 and 1/100 of LD_{50} has gonado- and embryotoxic action, which prevents its use on rapidly ripening crops.

Milbex is produced in the form of a 50% wettable powder (with an equal content of each of its components). It is recommended for controlling spider mites on cotton at a rate of 2-2.5 kg (1-1.25 kg a.i.) per hectare. To ensure a high effectiveness of the treatments, the acaricide must completely cover the leaves of the cotton plants. This is achieved the best of all by using helicopters, tractor-mounted compressed-air sprayers, and machines with a vertical suspension of the nozzles. Milbex may be used on cotton not later than 20 days before harvesting.

The pilot use of milbex has been permitted on fruit trees, including citrus ones, and berries to monitor mites in a concentration of 0.1-0.2% at a rate of 2-2.5 kg (1-1.25 kg a.i.) per hectare. The harvest time for all crops is 20 days.

Bromopropylate (Neoron, Acarol)

The active ingredient is isopropyl 4,4′-dibromobenzilate (bromopropylate):



The pure substance is a cream-coloured powder melting at 77 °C. It dissolves poorly in water (less than 5 mg/litre at 20 °C), and well in most organic solvents. It has a considerable volatility.

Bromopropylate is stable when stored in neutral media. Alkalies and acids decompose it to non-toxic products.

It persists in the soil for a long time, but migrates slowly along the profile. The persistence and migration depend on the properties of the soil.

Bromopropylate is relatively stable on plants, and its residues are detected in the leaves even after 40 days following treatment. The substance decomposes very slowly. The losses of the active ingredient on a plant are mainly explained by its spreading upon growth

of the vegetative matter and by the action of meteorological factors (the wind, atmospheric precipitation, solar radiation).

The acaricide does not burn plants in its recommended concentrations.

Bromopropylate is a contact acaricide exhibiting a penetrating and fumigational action. The duration of the protective action reaches 8-10 weeks on isolated plots, and two or three weeks in conditions of a close source of inhabitance by mites. Bromopropylate has a high initial toxicity (extermination of mites—84.5-99.4%) and a good ovicidal action. It is highly effective in controlling mites, including those resisting organophosphorus and organochlorine acaricides. For a high effectiveness, the entire surface of the plant being protected must be sprayed very thoroughly.

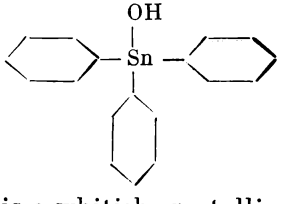
Bromopropylate has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 5000 mg/kg). Its dermal and chronic toxicities are slight. When it gets into an animal's organism, the substance during the first two days is excreted with the feces and the urine (60-80% of the total amount of the substance with the feces). An analysis of the excreted products has shown that from 60 to 90% of the bromopropylate is excreted in the unchanged form. Among the metabolites of bromopropylate, 4,4′-dibromobenzyl acid having no appreciable toxicity has been identified.

Bromopropylate is marketed in the form of 25% and 50% emulsifiable concentrates and is recommended for pilot application on cotton against spider mites in a system of alternation with other acaricides. The rate of use of the 25% compound is 3-4 kg/ha, of the 50% compound is 1.5-2.0 kg/ha, and of the active ingredient, 0.75-1.0 kg/ha. The harvest time in the treatment of cotton with bromopropylate is 20 days.

The pilot application of new specific acaricides differing in their chemical structure and mechanism of action—cyhexatin and propargite—has been permitted on cotton from 1977 for inclusion in a system of alternation of acaricides.

Cyhexatin (Plictran)

The active ingredient is tricyclohexyltin hydroxide:



In the pure form, it is a whitish crystalline nearly odourless nonvolatile powder melting at 195-198 °C. It dissolves poorly in water

(less than 1 mg/litre at 25 °C) and organic solvents, and is chemically and thermally stable. It decomposes on treated surfaces under the action of ultraviolet radiation.

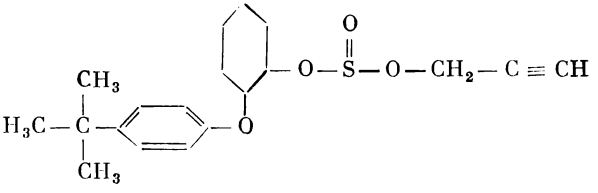
It has no phytotoxic properties.

Cyhexatin is a specific contact acaricide with a moderate initial toxicity (lower than that of milbex) and with repellant, antifeeding properties. Spider mite females do not lay eggs on a treated surface, while bollworms refuse to feed after plant treatment. The duration of the acaricide's protective action is 20 days and more. Cyhexatin is moderately toxic to humans and animals (LD_{50} for rats is 235-650 mg/kg) and has a local dermal irritating action.

Its pilot use is allowed with only a single treatment during a season with a 25% wettable powder. The rate of use is 2-2.5 kg (0.5-0.62 kg a.i.) per hectare against spider mites, especially in zones with resistance of the mites to organophosphorus acaricides, and not later than 30 days before harvesting.

Propargite (Omite, Comite)

The active ingredient is 2-(4-tert-butylphenoxy)cyclohexyl-2-propynyl sulphite:



The technical product is a dark brown liquid sparsely soluble in water and well soluble in organic solvents.

The substance has no negative effect on plants in the recommended concentrations.

Propargite is a specific contact acaricide with a moderate protecting effect (up to 15 days). It is non-toxic to entomophags and bees. It is superior to dicofol and dimethoate in its action on mites, and is identically effective in controlling mites sensitive to organophosphorus compounds and those resistant to them.

It has a low toxicity to humans and animals (LD_{50} for rats is 1800-2000 mg/kg).

A 30% wettable powder and a 57% emulsifiable concentrate are recommended for pilot application, at a rate of 2.5-3 kg (0.7-0.9 kg a.i.) and 1.5-2 kg (0.8-1.1 kg a.i.) per hectare, respectively. Only a single treatment of crops 45 days prior to harvesting is permitted.

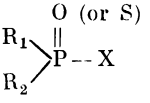
6.1.2. Organophosphorus Compounds

Organic phosphorus compounds are one of the most important groups of modern pesticides. The widespread use of these compounds is due to their high insecticidal and acaricidal activity, the broad spectrum and rapidity (high initial toxicity) of action on pests, their low stability in biological media, to their decomposition with the formation of products non-toxic to humans and animals, their relatively rapid metabolism in the organisms of animals and the absence of an ability to be deposited in them, to the systemic action of a number of toxicants and in this connection to the smaller danger to entomophags, their low rate of use per unit of treated area, their rapid decomposition in the soil and water, and to their moderate toxicity to fish.

Among the negative features of most organophosphorus compounds is their high toxicity to humans and animals and the relatively rapid appearance of resistant populations of pests after the perennial use of substances of this group.

1. Mechanism of Action

Modern organophosphorus insecticides and acaricides are compounds of pentavalent phosphorus of the general formula



where R_1 and R_2 are alkoxyl, alkyl, or aryl radicals combined with alkoxyl ones, or dimethylamine groups, and X is a residue of a weak acid.

The bond of X with the phosphorus has an anhydride nature, and the substance itself—the properties of a phosphorylating agent. We can thus assume that a substance having such a structure, when getting into an organism, phosphorylates vitally important substrates. Indeed, it has been established that the enzyme contained in nerve tissues—acetylcholinesterase, which plays an exceedingly important role in the transmission of a nerve impulse, is such a substrate.

The fundamental structural element of an animal's nervous system is a nerve cell (neuron) (Fig. 6) whose designation is to receive, interpret, and transmit information in the form of nerve signals (impulses). The short and numerous branches (dendrites) of a neuron connected to the axons of other cells gather information, while the single long branch (axon) terminating in a bulb-shaped thickening (a synaptic platelet), transmits the information. Hence, a nerve impulse

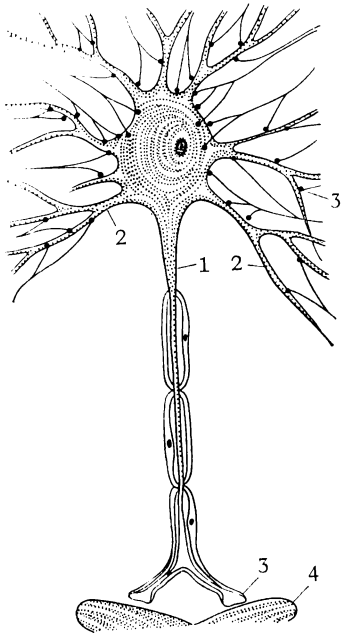


Fig. 6. Structure of a neuron:
1—axon; *2*—dendrites; *3*—synaptic platelets; *4*—muscle fibres

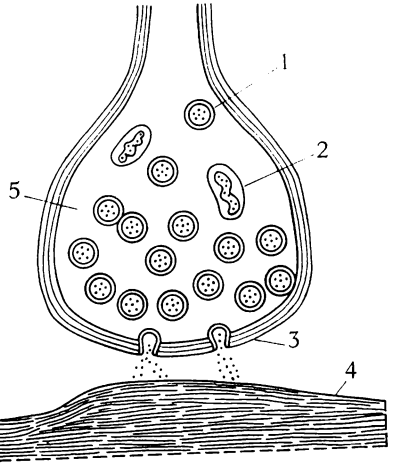


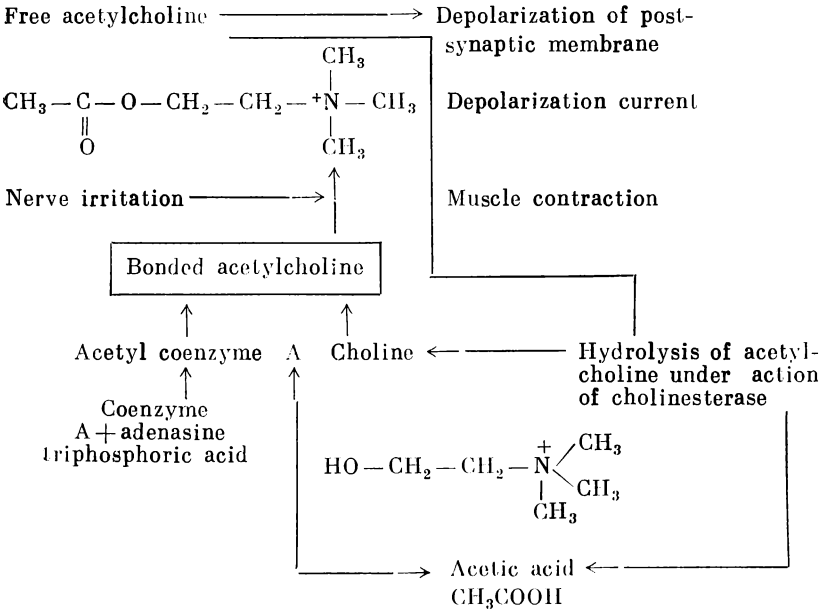
Fig. 7. Nerve-muscle synapse:
1—vesicles (synaptic vesicles); *2*—mitochondria; *3*—presynaptic membrane; *4*—postsynaptic membrane; *5*—synaptic platelet

in the form of an original electric signal travels along a neuron, always from a dendrite to the axon and further from the latter to a dendrite of another cell or to a muscular fibre.

The ending of a nerve and the membrane of another cell or muscle are separated by a synaptic cleft from 30 to 50 nm wide. The cleft is filled with a gel-like substance and has a tremendous electrical capacitance, therefore an electrical signal cannot pass through it. A nerve impulse is transmitted through the synaptic cleft with the aid of chemical substances (mediators or transmitters) secreted through the presynaptic membrane. Acetylcholine and noradrenaline are the most widespread transmitters. Synapses where a nerve impulse is transmitted with the aid of acetylcholine are called **cholinergic**, and those where noradrenaline is the mediator are called **adrenergic**. A nerve-muscle synapse is shown schematically in Fig. 7.

The free acetylcholine in the inactive form bound to proteins accumulates in the ending of a nerve in vesicles. The consumed acetylcholine is constantly replenished by its synthesis—by the acetyla-

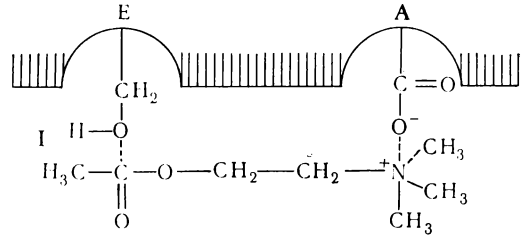
tion of choline. All the processes occurring when an impulse is transmitted through a cholinergic sinapse can be represented by the following diagram:



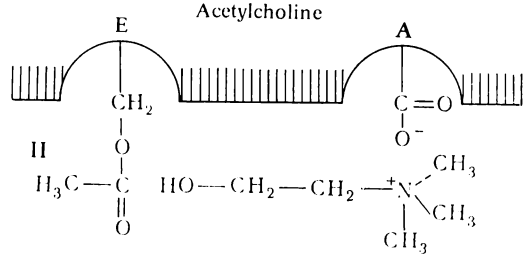
Hence, the process of synaptic transmission is an involved biochemical cycle of acetylcholine exchange. Acetylcholinesterase has an exceedingly important significance in this cycle because the inhibition of activity leads to the accumulation of free acetylcholine in the synaptic cleft. As a result, the normal passing of nerve impulses is disrupted, convulsive activity of the muscles sets in that transforms into paralysis, and other features of self-poisoning of the organism by surplus acetylcholine appear.

An active centre of acetylcholinesterase consists of two sections: an anionic one (A) containing an ionized carboxyl of asparaginic and glutamic acids, and an esterase one (E) containing a hydroxyl of serine. The acetylcholine decomposes in three steps: I—sorption of the acetylcholine on the anionic section that fixes a molecule of the transmitter on the surface of the enzyme and sharply increases the probability of a reaction; II—acetylation of the enzyme with the formation of choline; and III—desorption of the choline and hydrolysis of the acetylated enzyme; here the enzyme is regenerated, and acetic acid

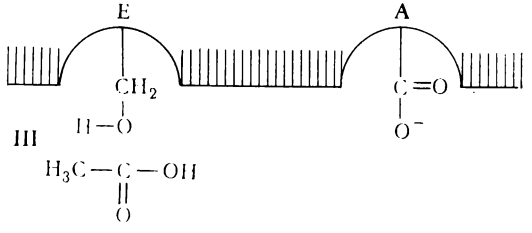
is evolved:



Acetylcholine



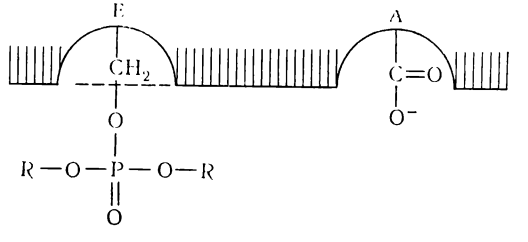
Choline



Acetic acid

The entire complicated process occurs exceedingly rapidly (in several milliseconds). An unfailing condition for the reaction to proceed is the strict polar and steric correspondence of the transmitter and the enzyme.

All organophosphorus insecticides imitate the ester part of acetylcholine and when they enter an organism react with the esterase section of the acetylcholinesterase:



Phosphorylation of the enzyme occurs with detachment of the acid residue X. The nature of X does not affect the structure of the inhibited enzyme, but acts strongly on the process of its inhibition. Organophosphorus substances carrying a charge in the acid residue are very active inhibitors of cholinesterase. For example, the action is amplified when the sulphur atom in the thioester radical is oxidized.

Unlike the acetylated enzyme, phosphorylized cholinesterase hydrolyzes very slowly (in several hours and even days). The explanation is the high hydrolytic strength of phosphorus esters and the need of breaking the alkyl-oxygen bond $O—CH_2$ in hydrolysis, which is not among the functions of cholinesterase. Consequently, the acetylcholinesterase is withdrawn from the sphere of action for a prolonged period, and acetylcholine accumulates in the synaptic clefts. The result is a sharp disruption of the functions of all organs having cholinergic innervation, and poisoning of the organism occurs.

The discovery of the mechanism of action of organophosphorus compounds made it possible to develop the fundamental principles of the directed synthesis of new substances and establish the causes of their selective action on an organism. Acetylcholine transmits nerve excitation in the organisms of both higher vertebrates and of insects and mites. This is why organophosphorus compounds are toxic to representatives of these groups. The degree of toxicity has major fluctuations, however, which is associated with the features of structure of the nervous system and the metabolism of animals.

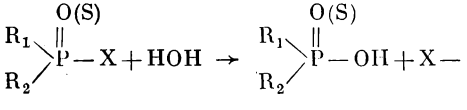
2. Transformation in Biological Media

Organophosphorus compounds have a high reactivity. This is why they readily enter into chemical reactions with various substances and, when getting into an organism, are involved in metabolic processes. The diversity of their structures explains very well the multiplicity and diversity of their metabolic transformations.

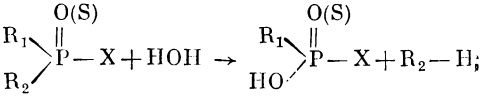
Non-Enzyme Reactions. *Hydrolysis.* All organophosphorus compounds readily hydrolyze in an alkaline medium with the formation of non-toxic products. Derivatives of phosphoric and phosphorothiolic acids are more liable to hydrolysis than phosphorothionates and phosphorodithioates.

At the same time, O-methyl derivatives of phosphoric acids are the least stable to hydrolysis.

The reaction mainly proceeds with breaking of the P—X bond and the formation of the relevant phosphoric acid:

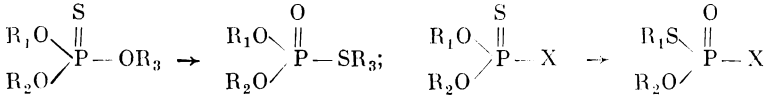


The reaction of hydrolysis along the P—R bond attended by a loss of toxicity is typical of some substances (dichlorvos):



A non-enzyme hydrolytic reaction may occur during the storage of the toxicants, in a working solution, on the surface of plants, and in the soil, and is accelerated in the presence of many amino acids, inorganic phosphates, and ions of chlorine, copper, and molybdenum.

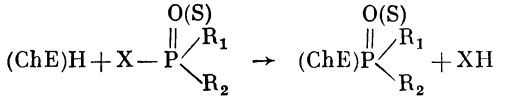
The *isomerization* (transformation of one isomer into another) of organophosphorus compounds is attended by a sharp increase in the anticholinesterase activity and, consequently, in the toxicity. But here the resistance to hydrolysis and the intactness of the substance in biological media diminishes. Two kinds of isomerization are encountered:



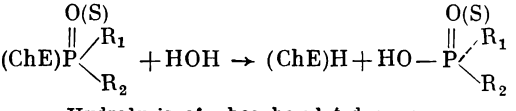
Such processes take place very actively at an elevated temperature, but are also noted in conventional conditions on the surface of plants and in the soil. Isomerization is encountered most often in phosphorothionates and phosphorodithioates.

Enzyme Reactions. The reaction of *phosphorylation* of cholinesterase is the main one among those entered into by organophosphorus compounds in an organism because the toxicity of a substance depends on its rate and the stability of the phosphorylated product formed.

The phosphorylation of an enzyme is attended by decomposition of the active ingredient because non-toxic compounds are formed after the hydrolysis of phosphorylated cholinesterase:



Phosphorylation of cholinesterase (ChE)



Hydrolysis of phosphorylated enzyme

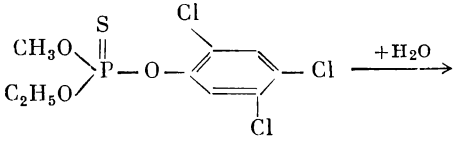
The phosphorylation of other enzymes (for example, aliesterase) also occurs in the organisms of warm-blooded animals and insects.

It is attended by a rapid loss in the toxicity of the organophosphorus insecticides because the phosphorylation products very rapidly hydrolyze with the formation of dialkyl phosphates.

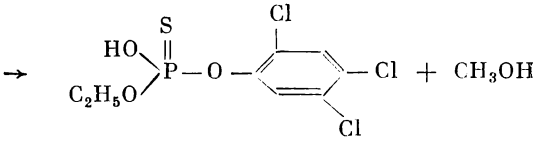
Hydrolytic decomposition is the most frequently encountered way of enzymatic transformation of organic phosphorus compounds in living organisms. The place of detachment may vary and depends on the structure of the substances.

Phosphatase Action. A molecule of an organophosphorus substance contains two kinds of groups whose bond with the phosphorus atom may be broken by phosphatase: the electronegative group X forming a relatively unstable anhydride bond with the phosphorus, and an alkoxy group having a stronger bond with the phosphorus. The hydrolysis of organic phosphorus compounds by phosphatases is the main metabolic way leading to a complete loss of toxicity in the organisms of humans, warm-blooded animals, insects, and plants. Phosphatase most frequently attacks the P—X bond. The reaction follows the same scheme as in chemical hydrolysis.

The bond P—O(Alk) is broken much more seldom and sometimes at later stages of metabolism after decomposition of the molecule along the P—X bond. For some substances, for example for bromophos, trichlorometafos-3, and dichlorvos, such a reaction is the first reaction of hydrolysis:



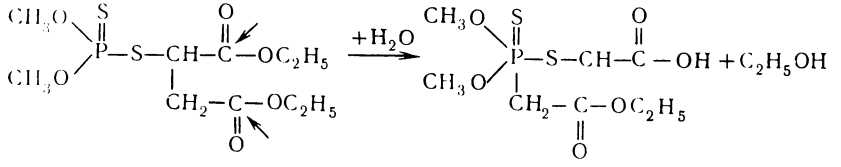
Trichlorometafos-3



Dimethyl phosphates enter into this reaction more readily than diethyl phosphates, but it is sometimes observed in the latter too. In all cases, the detachment of an alkoxy group from a phosphorus atom leads to the detoxication of the organophosphorus compounds. This process is encountered to a greater extent in warm-blooded animals and insects, and less often in plants.

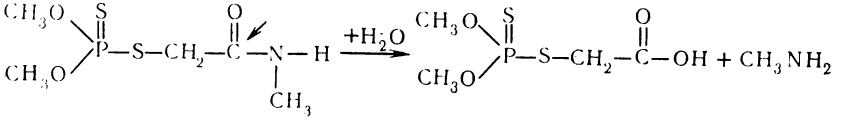
Carboxyesterase Action. All organophosphorus compounds containing an ester group are decomposed by carboxyesterases in the or-

ganism along an ester bond:



The result is detoxication of the compound because the formed substances have an anionic nature, and the charge of the anion prevents the reaction with cholinesterase. This reaction proceeds most rapidly in the organism of humans and warm-blooded animals and in a number of cases determines the selectivity of action of the insecticides.

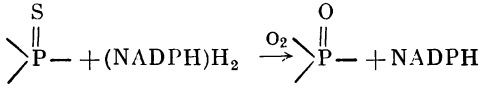
Amidase Action. In organic compounds of phosphorus containing a carbamide group, amidase hydrolysis with the formation of nontoxic products of an anionic nature is often the primary reaction of metabolism:



The toxicity of substances like dimethoate depends directly on the activity of the amidases in an organism. Their selective toxicity with respect to insects is explained by the differences in the activity of the amidases.

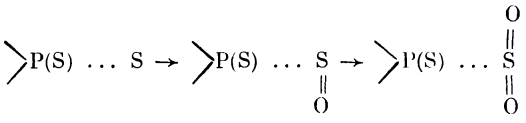
The **oxidizing** way of exchange of organophosphorus compounds is very widespread and can proceed in different directions depending on the structure of a substance. The oxidation of these substances is almost always attended by an increase in the anticholinesterase activity and in the toxicity of the compounds.

Oxidation to phosphates is a feature of all phosphorothioates and dithioates:



and occurs in all organisms (insects, mammals, plants) with the participation of microsomic enzymes and reduced pyridine nucleotides. The toxicity of the compounds grows very sharply, but simultaneously the solubility in water increases and the resistance to hydrolysis diminishes.

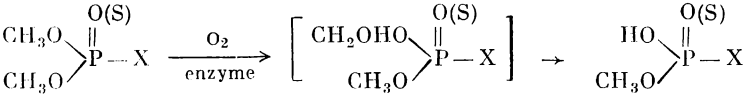
The *oxidation of thioester sulphur* is characteristic of organophosphorus compounds containing such sulphur. This reaction is encounteredmore often in plants and insects, and more rarely in animals. The formed sulphoxides and sulphones have a high anticholinesterase activity, but the toxicity of the substances does not always grow. In the general form, the reaction can be represented as follows:



The oxidation of the thioester sulphur in an organophosphorus compound results in the appearance of a partial positive charge, which ensures better reaction with the acetylcholinesterase. This is why the anticholinesterase activity grows. The charged molecules, however, penetrate poorly through the lipoid membranes. Hence, the amount of the substance entering the nervous system may decrease, and its toxicity to the organism does not increase.

N-dealkylation is mainly characteristic of phosphoric acid esters having (X)N-alkylamide groups in the anhydride part of the molecule, and of the amides of these acids. The reaction proceeds in two steps with the participation of enzymes and is attended by an increase in the anticholinesterase activity. The formed N-hydroxyalkyl derivatives are just as toxic as the starting substance and are quite stable in biological media.

O-dealkylation is a feature of many organophosphorus compounds and plays a major role in the process of their metabolism. The reaction proceeds with the participation of the oxidase microsomic system bound to NADPH (nicotinamide adenine dinucleotide phosphate). The products of this reaction are considerably less toxic and less resistant to hydrolysis than the starting substance. Dimethylphosphates (fenthion and the like) are the most liable to O-dealkylation:

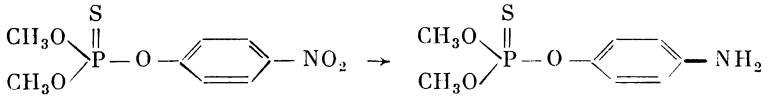


The dealkylation of acids of phosphorus is apparently the main reaction proceeding in an animal's organism that competes with the phosphorylation of cholinesterase. When this process predominates, the toxicant decomposes before it reaches the place of its action, i.e. the toxicity of the substance diminishes. This assumption, advanced in 1961 by the Soviet scientist N. Melnikov, is receiving substantial confirmations at present.

O-dealkylation can proceed in a living organism under the action of enzymes not causing oxidation—alkyltransferase associated with the reduction of glutathione.

The three dealkylation reactions are encountered much more seldom than hydrolysis and oxidation, and are characteristic only of a few organophosphorus compounds.

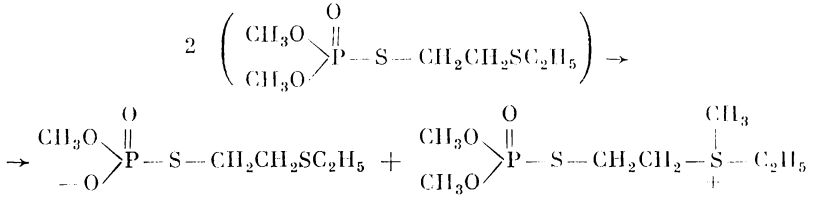
The **reduction** way of transformations has been studied quite well for parathion-methyl:



The aminophenyl derivatives formed are less toxic to animals.

In insects' organisms, the reaction of dehydrochlorination of trichlorfon takes place with the formation of the more toxic substance dichlorvos.

Finally, some organic compounds of phosphorus are capable of entering into a reaction of intermolecular realkylation in which one molecule of a substance is alkylated at the expense of another one:



The sulphonic compound formed has a considerably higher activity.

In a living organism, the same compound may be involved in the most diverse reactions, as a result of which a multitude of various exchange products are formed. It is general knowledge that some reactions lead to a substantial activation of organophosphorus compounds, while others result in their detoxication. The ratio of the rates of these reactions may vary in different species of animals. This is what most frequently underlies the selective toxicity of the organic compounds of phosphorus.

3. Action of Organophosphorus Insecticides on Insects

The toxic action of organophosphorus compounds on insects is due to inhibition of the activity of acetylcholinesterase in the cholinergic synapses of the nervous system. Upon penetrating into an organism through the integuments of an insect, or through the alimentary tract or the respiratory tracts, the insecticide together with the hemolymph stream reaches the nervous system. Since cholinergic synapses have been detected in insects only in their central nervous system, the action of organophosphorus compounds violates the trans-

mission of nerve impulses between the associative neurons in the ganglia. At the same time, the peripheral system, particularly nerve-muscle connections, is not harmed because *l*-glutaminic acid is the mediator in synapses of this system.

When organophosphorus compounds enter the organism of an insect, the activity of the acetylcholinesterase sharply drops. Indications of poisoning appear very rapidly and express themselves in hyperactivation of the insect and tremors of its appendages. Next paralysis sets in ending in death. Most organophosphorus insecticides and acaricides have a high initial toxicity, and pests perish during the first few hours after treatment.

Substances of this group are good for controlling larvae and adult individuals of pests, but their ovicidal action is weak, which is associated with the low permeability of egg shells. Oil solutions of some organophosphorus compounds penetrate quite well into the eggs of insects and mites, causing their death. The activity of an embryon's cells and its growth are not violated, but acetylcholine accumulates in the embryon. The larva dies owing to its inability of moving when it leaves the egg. This is why plantings should be treated with oil formulations of such a kind not long before the larvae hatch from the eggs.

Upon the perennial use of organophosphorus insecticides and acaricides, specific resistance appears in insects and mites.

Cases are known of the appearance of individual (to one toxicant), group, and cross resistance.

Specific resistance to organophosphorus compounds appears more rapidly in the species of insects that produce several generations in a single season. Resistance is known to have appeared in aphids, houseflies, cockroaches, mosquitoes, and some other species of insects. But the most dangerous is the development of resistance in phytophagous mites. The economical harm from this phenomenon is very great, especially in cotton-growing regions.

The main way of dealing with acquired resistance and preventing it is the use of a system of alternating insecticides and acaricides with different mechanisms of action.

4. Action on Humans and Warm-Blooded Animals

Organophosphorus compounds are mainly highly and moderately toxic to humans and warm-blooded animals. Upon entering the human organism, they affect the cholinergic synapses of the central nervous system and the peripheral nerve-muscle connections.

Many compounds of this group have an acute and moderate chronic toxicity that manifests itself upon the frequent introduction of toxic or sublethal doses. The high activity of phosphatases, carboxyesterases, and amidases in the organisms of warm-blooded animals

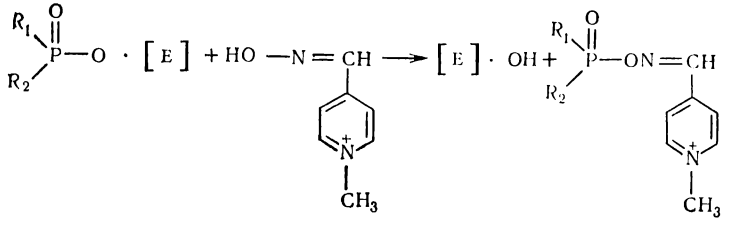
results in the rapid decomposition of organophosphorus compounds into non-toxic water-soluble products with their following excretion with the urine. This is why functional cumulation and inhibition of the activity of cholinesterase are mainly observed in chronic poisoning.

The dermal toxicity of organophosphorus insecticides is not high, but toxicants such as metasystox and parathion-methyl are highly toxic when they get onto the skin.

Recent years have seen the discovery and introduction of a considerable number of insecticides and acaricides with a low toxicity to humans and warm-blooded animals.

Two kinds of antidotes are chiefly used to treat cases of poisoning by organophosphorus compounds: cholinolytic means and cholinesterase reactivators. The action of the former is based on blocking the choline receptors of the postsynaptic membrane. This creates an obstacle to the toxic action on them of the acetylcholine accumulating in the synapses under the action of these insecticides. The action of the second antidotes consists in reactivating the inhibited cholinesterase.

Among the antidotes of the first kind, great favour has been given to atropine. Among those of the second kind, dipyroxym is an effective reactivator of cholinesterase. Reactivation of the enzyme follows the scheme:



The joint use of antidotes of both kinds is the most effective for treating heavy forms of poisoning by organophosphorus compounds.

5. Persistence in Soil and Action on Plant Being Protected

Organophosphorus insecticides, owing to their low chemical and thermal stability, rapidly decompose in the environment (soil, water, surface of plants) into non-toxic products. Decomposition in the soil occurs with the active participation of microorganisms. The process is sharply inhibited in sterilized soil. The persistence of modern organophosphorus insecticides in the soil does not exceed one month, therefore the danger of their residues contaminating fodder

and food products through the roots is reduced to a minimum. In addition, most insecticides of this group decompose in the plants.

In their recommended doses, the organic compounds of phosphorus do not burn plants and do not inhibit their growth and development. When these doses are exceeded insignificantly, many toxicants (parathion-methyl, trichlorometafos-3) damage the leaves, and especially the flowers and buds. No stimulation of the growth processes is observed. A negative influence on the quality of the products has not been recorded.

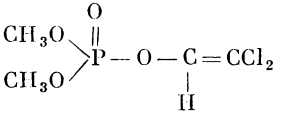
The processes of decomposition of organophosphorus compounds in plants proceed very actively, and even the most stable of them decompose in 30-40 days. When the harvest time is observed, the residues of these insecticides in products are either not detected at all or do not exceed the tolerance level.

6. Phosphoric Acid Derivatives

Mixed esters of phosphoric acid have a high insecticidal and acaricidal activity. Esters, one of whose radicals has an acid nature such as dialkylaryl phosphates, dialkyl fluorophosphates, and amides of fluorophosphoric acid, are especially active. The maximum toxicity of the mixed esters of phosphoric acid belongs to the diethyl derivatives. Dimethyl phosphates are less toxic to insects and humans because they hydrolyze in biological media more rapidly and, having a high alkylating ability, react with various compounds to form monoalkyl phosphates. The mixed aliphatic-aromatic esters of phosphoric acid, however, owing to their high toxicity to man, do not find practical use in agriculture. Halogen-containing esters of phosphoric acid and enol phosphates have a somewhat lower toxicity. They are used in medicine, in the veterinary science, and in plant growing.

Dichlorvos (DDVP, DDVF, Dichlorphos)

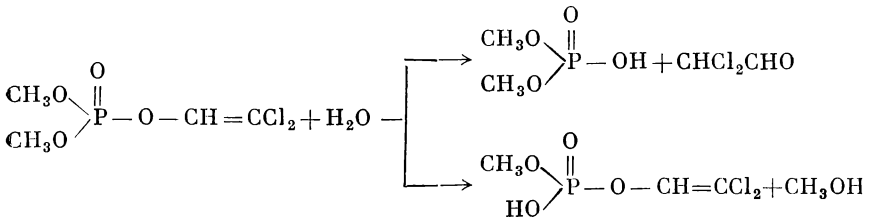
The active ingredient is 2,2-dichlorovinyl O,O-dimethyl phosphate:



In the pure form, it is a colourless to amber highly volatile liquid with an aromatic odour boiling at 74 °C. Its volatility is 145 mg/m³ at 20 °C. It dissolves well in most organic solvents, and poorly in water (1%).

Dichlorvos has a low chemical stability and is readily hydrolyzed in water and in alkaline solutions with the formation of products

having a low toxicity: dimethylphosphoric acid, 2,2-dichlorovinyl O-methyl phosphate, dichloroacetaldehyde, and methyl alcohol:



Such reactions proceed when a toxicant is stored in moist conditions, on treated surfaces, inside plants, in water basins, and in an animal's organism, and to a great extent determine the stability and toxicity of dichlorvos.

The persistence of the toxicant on treated inert surfaces depends on the temperature and humidity of the air. On porous surfaces (grain, walls), it is about 14 days, on glass and metal—24 hours. The concentration of dichlorvos in air after the use of its aerosol rapidly drops (by more than one-third during the first 20 minutes) and reaches a minimum in from two to five hours. This allows aerosol formulations to be used to control insects in dwellings and auxiliary premises.

Dichlorvos penetrates very well into the tissues of plants, but exhibits only a penetrating action because of the rapid decomposition of the active ingredient. Residues of the insecticide remain in fruits and berries from two to five days. It has no phytotoxic action.

Dichlorvos is an insecticide and acaricide having short-time action with a high initial toxicity. It has contact, intestinal, and fumigational effects. It is highly toxic to mites, aphids, young larvae and adult individuals of *Lepidoptera* and *Diptera*, and has an ovicidal action. The insects are exterminated in several minutes, especially when the substance enters through the respiratory tracts. The triple effect of the toxicant considerably diminishes the probability of resistant races of pests appearing. Owing to its short-time action, not over three days, it is not used as an acaricide.

Dichlorvos is highly toxic to bees and entomophags. It is also highly toxic to humans and animals (LD_{50} for rats is 65 mg/kg) and has an acute dermal and very acute inhalation effect. In the organism of a mammal, it rapidly decomposes into non-toxic products, the reactions of hydrolysis of the P—O(Alk) and P—X bonds taking place. The products recovered are dimethyl and methyl phosphoric acids, dichloroethyl alcohol, dichloroacetic acid, and H_3PO_4.

The industry markets a 50% emulsifiable concentrate of dichlorvos.

The formulation is used in apple and pear orchards to control leaf miners, apple moths, aphids, and psillids in a concentration of 0.1-0.2%; on cherry and plum trees to control cherry fruit flies—0.2-0.3%, on small-fruit patches to control curr nt flies, black-currant leaf and big-bud mites—0.2%; in citrus orchards to control citrus red mites, cushion scales, white flies, mealybugs, and wax scales (mobile primary larvae)—0.2-0.3%; on tea plantations to control tea moths—0.25%; on grapevines to control European grape moths—0.2%, and on cabbage to control leaf-eating caterpillars—0.2-0.3%. The rate of use of the formulation is 1-18 kg (0.5-9 kg a.i.) per hectare. Owing to its short-time action on pests, dichlorvos should be sprayed twice during the period of large-scale appearance of insects of each generation.

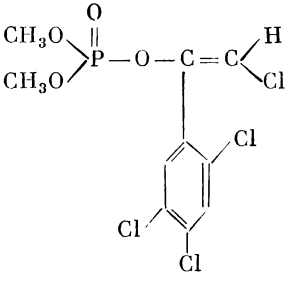
The technical effectiveness of dichlorvos is very high—95-100% of the pests are eradicated.

The harvest time for fruit orchards, grapevines and vegetable crops is 10 days. The tolerance level of dichlorvos in grain is 0.3, and on grapes and apples, 0.05 mg/kg; no residues of the insecticide in flour and cereals are tolerated.

Only tea-shrub plantations where the leaves are not being gathered may be treated.

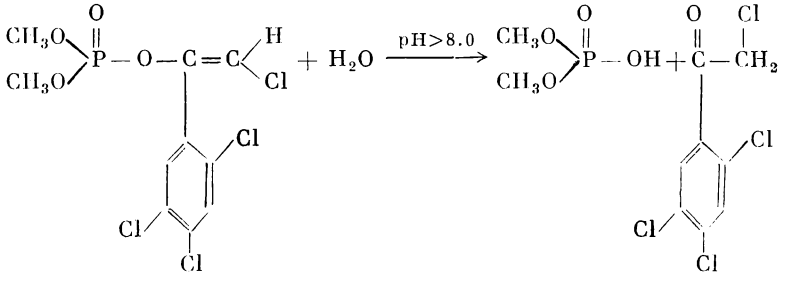
Tetrachlorvinphos (Gardona)

The active ingredient is 2-chloro-1-(2,4,5-trichlorophenyl) vinyl dimethyl phosphate:



It is a white crystalline substance poorly soluble in water (11 mg/litre at 20 °C) and most organic solvents and melting at 97-98 °C. Its volatility is low. It has a very high thermal and moderate chemical stability, but in an alkaline medium it hydrolyzes with the formation of dimethylphosphoric acid and 2,2′,4′,5′-tetrachloroaceto-

phenone:



The toxicant persists on treated surfaces from 12 to 15 days; when it penetrates into the tissues of plants, it rapidly decomposes into non-toxic products. No burns were found on plants when the formulations were tested. Only cotton, cantaloupes, grapevines, and tobacco plants were found to be more sensitive, but burns on the leaves were noted when oil emulsifiable concentrates were used.

Tetrachlorvinphos is a contact and stomach insecticide with a high initial toxicity and a moderate duration of its protective effect. It is highly toxic to adults and larvae of *Lepidoptera*, *Diptera*, and beetles, but does not virtually act on sucking pests, especially on mites. After application of the toxicant, a growth in the population of phytophagous mites is noted.

This insecticide is moderately toxic to bees and predatory insects. In this connection, tetrachlorvinphos is prospective for use in integrated systems of control.

The substance relates to compounds with a low toxicity to humans (LD_{50} for rats is 2955 mg/kg) with a slight cumulative effect (functional cumulation). It has a slight dermal and inhalation toxicity. It rapidly decomposes in human and animal organisms and is excreted with the urine. Its regular introduction during four months into test animals, however, resulted in lowering of the activity of the cholinesterase of the blood and in violation of the functional state of the liver and central nervous system.

The metabolism of tetrachlorvinphos in biological media proceeds rapidly in two directions: hydrolysis with the formation of dimethylphosphoric acid and 2,2′,4′,5′-tetrachloroacetophenone, and O-demethylation to desmethyl tetrachlorvinphos with the following hydrolysis (Fig. 8). The ratio and rates of these reactions vary depending on the kind of organism. This is assumed to determine the selectivity of the insecticide.

A 50% or a 75% wettable powder of tetrachlorvinphos is used: in apple orchards against apple worms at a rate of the formulations of 1.6-4 and 1.1-2.6 kg (0.8-2 kg a.i.) per hectare; on grapevines against European grape moths—1.2-3 and 0.8-2 kg of the formulation

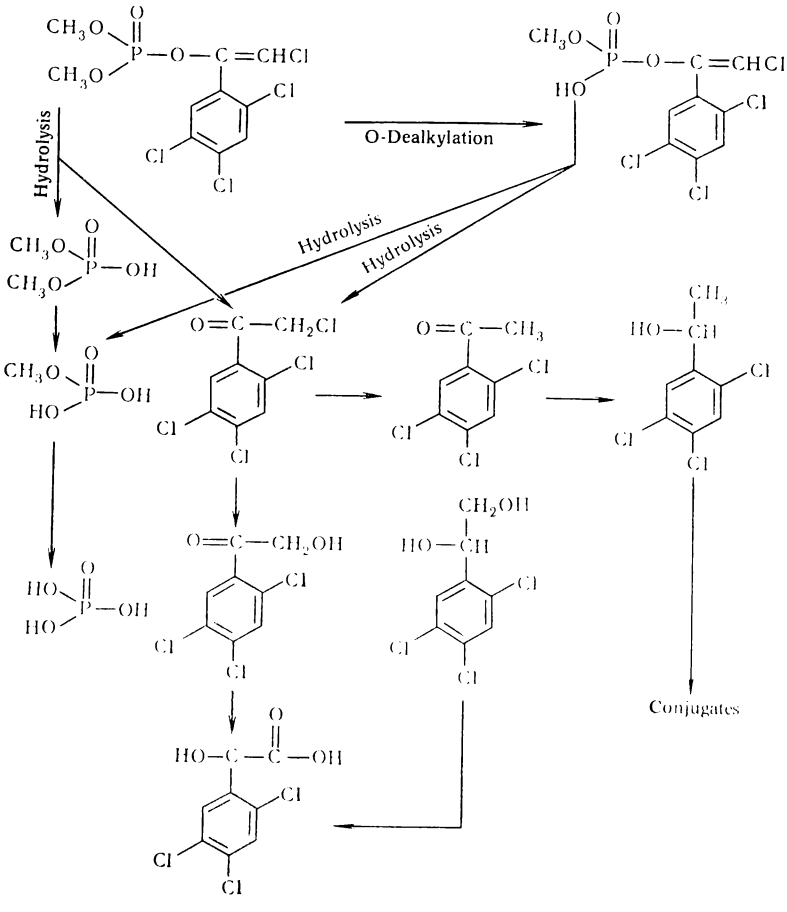


Fig. 8. Diagram of metabolism of tetrachlorvinphos

(0.6-1.5 kg a.i.) per hectare; on cherry, plum, and pear trees against cherry fruit flies, moths, and sawflies, on gooseberries against sawflies and gooseberry fruit worms—1.6-3 and 1.1-2 kg (0.8-1.5 kg a.i.) per hectare; on cabbage against large and small white butterfly caterpillars and cabbage moths—1.5-2 and 1.1-1.3 kg (0.7-1 kg a.i.) per hectare; on cotton against bollworms—2.5-3 and 1.8-2 kg (1.3-1.5 kg a.i.) per hectare; on hops against a collection of leaf miners and beetles—2.4-4 and 1.6-2.7 kg (1.2-2 kg a.i.) per hectare; and on strawberries—1.2-2 and 0.8-1.3 kg of the formulation (0.6-1 kg a.i.) per hectare.

Widespread tests of tetrachlorvinphos in monitoring apple worms showed its high effectiveness. Lowering of the damage to the har-

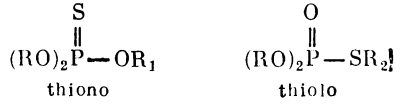
vested crop was 93-99% against 57-97% when carbaryl was used. This was attended by a sharp increase in the yield of marketable grades, especially of the first (highest) one.

The last treatment of crops with this insecticide is to be not later than 20 days before harvesting.

The tolerance level of tetrachlorvinphos in fruits and vegetables is 0.8 mg/kg.

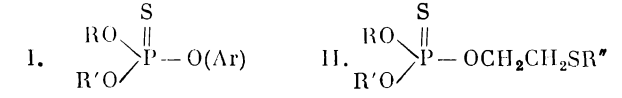
7. Phosphorothioic Acid Derivatives

Substances of this group find widespread use in agriculture owing to their high insecticidal and acaricidal activity and their lower toxicity to man than phosphates. The derivatives of phosphorothioic acid can be in the form of either of two isomers:



Thiolo derivatives are powerful inhibitors of cholinesterase and are therefore more toxic to humans and warm-blooded animals than thiono ones. When heated or acted upon by certain reactants, thiono isomers regroup into thiolo ones. Such a process may occur on the surface and inside plants, and also when storing formulations.

The main compounds used as insecticides are mixed esters of phosphorothioic acid:



where R, R′ = lower aliphatic radical
R″ = aliphatic, aromatic, or heterocyclic radical
Ar = aromatic or heterocyclic radical containing various substituents in the ring.

Esters of phosphorothioic acid in which R and R′ are either two ethyl radicals or one methyl and one ethyl radical have the maximum activity. O,O-dimethyl phosphorothionates, which find a greater use, have the lowest toxicity to humans and warm-blooded animals.

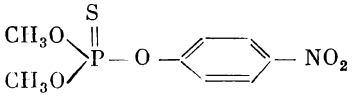
Among the mixed esters of general formula I, substances containing a nitrogroup (parathion-methyl), halogens, a cyano or a sulphide group in position 4 of the benzene ring have the highest insecticidal activity. The introduction of a second substituent into the aromatic radical lowers the toxicity of the substance to mammals without changing its insecticidal properties (fenitrothion). Compounds containing substituents in positions 2,4,5 (trichlorometafos-3)

are also good insecticides. The replacement of an aromatic radical with a heterocyclic one also yields active insecticides (diazinon).

Most compounds of general formula II are systemic insecticides and acaricides highly toxic to mammals. An increase in the number of methylene groups between the phosphorus and sulphur atoms to more than four sharply lowers the activity of the compound. Oxidation of the sulphur to sulphoxide and sulphone increases the toxicity of the substance. Owing to the high toxicity of substances of this group to humans and their prolonged persistence in plants, their use is restricted.

*Parathion-Methyl (Metafos, **Methyl Parathion,** Wofatox)*

The active ingredient is O,O-dimethyl-O-4-nitrophenyl phosphorothioate:



In the pure state, it is a white crystalline substance melting at 35-36 °C, poorly soluble in water (55-60 mg/litre at 25 °C) and in paraffin hydrocarbons (alkanes), and well soluble in most organic solvents. It has a moderate volatility of 0.14 mg/m³ at 20 °C and of 0.53 mg/m³ at 30 °C.

Parathion-methyl is a substance with a low thermal and chemical stability: when heated, it transforms completely into the relevant thiolo isomer with the following rapid decomposition into non-toxic products. In an alkaline medium, parathion-methyl rapidly hydrolyzes to O,O-dimethylphosphoric acid and 4-nitrophenol. It is a strong alkylating agent and can methylate sulphides, amines, thiourea, and other compounds. The reactions of hydrolysis and demethylation underlie the process of detoxication of this insecticide in organisms. The rate of the reactions is boosted considerably under the action of enzymes.

Owing to its low stability, parathion-methyl rapidly vanishes from treated surfaces, especially plants, from the soil and water basins. Decomposition of the toxicant in the soil proceeds with the participation of microorganisms, and in seven days 95% of the introduced substance decomposes.

When it gets onto a plant, parathion-methyl can enter the leaves and exhibit penetrating action. Phosphatases cause the compound to rapidly hydrolyze, and in two or three days 80-90% of it decomposes. The only exception here are citrus trees, in whose leaves parathion-methyl remains over seven days. In addition to hydrolysis

with the formation of less toxic products, in the tissues of plants this insecticide is oxidized to paraoxon-methyl whose toxicity is higher than that of the starting substance. The resistance of paraoxon-methyl to hydrolysis is not high, however, and this is why its residues are not detected in plants.

In its recommended concentrations, parathion-methyl does not burn the leaves of plants, but causes burning of the buds and flowers. Specific sensitivity of some species of plants to this insecticide has been noted.

Parathion-methyl is a contact insecticide and acaricide with a high initial toxicity and a short protective action (3-5 days); it also kills insects when it is ingested together with food and through the respiratory tracts. It is highly toxic to sucking insects and to *Coleoptera*. Owing to its deep action, parathion-methyl can exterminate mining pests and sucking insects on the opposite side of a leaf. When it is used perennially, races of insects and mites appear that are resistant to organophosphorus compounds. Owing to their short protective action in controlling mites, it is recommended to use parathion-methyl formulations in combination with specific acaricides.

Parathion-methyl is highly toxic to humans and warm-blooded animals (LD_{50} is 15-20 mg/kg) and has acute dermal toxicity. When it is ingested into a mammal's organism, phosphatases rapidly hydrolyse parathion-methyl to dimethyl phosphorothioic acid and 4-nitrophenol. Simultaneously, the nitro group of the benzene ring is reduced to an amino group, and the alkoxy groups are demethylated, as a result of which the substance loses its anticholinesterase activity. For this reason upon the daily ingestion into a human organism of small doses of parathion-methyl, it does not accumulate in the tissues, but experiences functional cumulation. Owing to the high toxicity of parathion-methyl and its ability of cumulation, no residues of it in food products are tolerated.

Several formulations of parathion-methyl are used in agriculture.

A 20% emulsifiable concentrate and a 30% wettable powder in a concentration of 0.1-0.3% are used on fruit and berry crops (apples, pears, plums, cherries, gooseberries, currants, strawberries) to control aphids, mites, psyllids, leaf hoppers, mobile primary larvae of scales, pseudocaterpillars of sawflies, caterpillars of leaf miners, apple fruit and cherry shoot moths; on citrus fruits to control citrus whiteflies, mobile primary and secondary larvae of citricola and Japanese wax scales and laurel leaf hoppers; on tobacco, sunflowers, castor-bean plants, and mustard to control a collection of pests. The rate of use of the formulations is 0.5-5.0 and 0.35-3 kg (0.1-1 kg a.i.) per hectare, respectively.

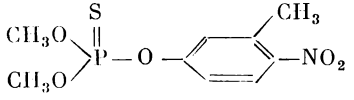
The pilot use of a 20% emulsifiable concentrate and a 30% wettable powder of parathion-methyl is allowed for controlling locusts at a rate of 0.2-0.4 kg a.i./ha.

In monitoring grain crop pests, aerial spraying is the rule with the working liquid used at a rate of 25-50 litre/ha. In this case, the concentration of the working solution is increased to 0.5-1.5%.

The harvest time of parathion-methyl for orchards, grapevines, vegetable, citrus, and melon crops is 30 days, for cereal and leguminous crops—15 days, and alfalfa—30 days. It is prohibited to use an emulsifiable concentrate or a wettable powder of parathion-methyl on green peas and asparagus beans, on berry plantations after blossoming, and in orchards during blossoming.

Fenitrothion (Metathion, Methylnitrophos, Sumithion)

The active ingredient is O,O-dimethyl-O-(3-methyl-4-nitrophenyl) phosphorothioate:



In the pure form, it is a brownish-yellow liquid with an unpleasant odour boiling at 95 °C. Its volatility is 0.09 mg/m^3. It dissolves well in organic solvents; its solubility in water is 30 mg/litre.

In its chemical properties, fenitrothion does not differ from parathion-methyl, but the rate of its hydrolysis by water and alkalies is considerably lower: in an alkaline medium at 20 °C it hydrolyses by 85% only in 49 days.

The persistence of the toxicant on treated objects depends on the conditions of treatment and the properties of the object. On the porous surfaces or the walls of storage premises, fenitrothion persists during three to six months. In sterile and acidified water, it is very stable, whereas its half-life in river water in aerobic conditions is 50 hours, and in anaerobic ones, 30-40 hours.

A decisive role in the decomposition of this insecticide in the soil is played by aerobic bacteria, particularly *Bacillus subtilis*, which at a temperature of 37 °C decompose 50% of fenitrothion to its amino analogue during 24 hours. The metabolites discovered in the soil also include desmethyl derivatives of fenitrothion and its amino analogue, 3-methyl-4-nitrophenol, dimethyl phosphorothioic and phosphoric acids (Fig. 9). On an average, fenitrothion persists in the soil during 10-20 days.

When it gets onto a plant, fenitrothion rapidly penetrates into its tissues (over 50% of the total amount in 24 hours), but does not migrate along the vascular system, exhibiting only a penetrating effect. It decomposes in a plant quite actively in three main directions: hydrolysis to dimethyl phosphorothioic acid and 3-methyl-4-nitrophenol with the following conjugation of the latter with glucur

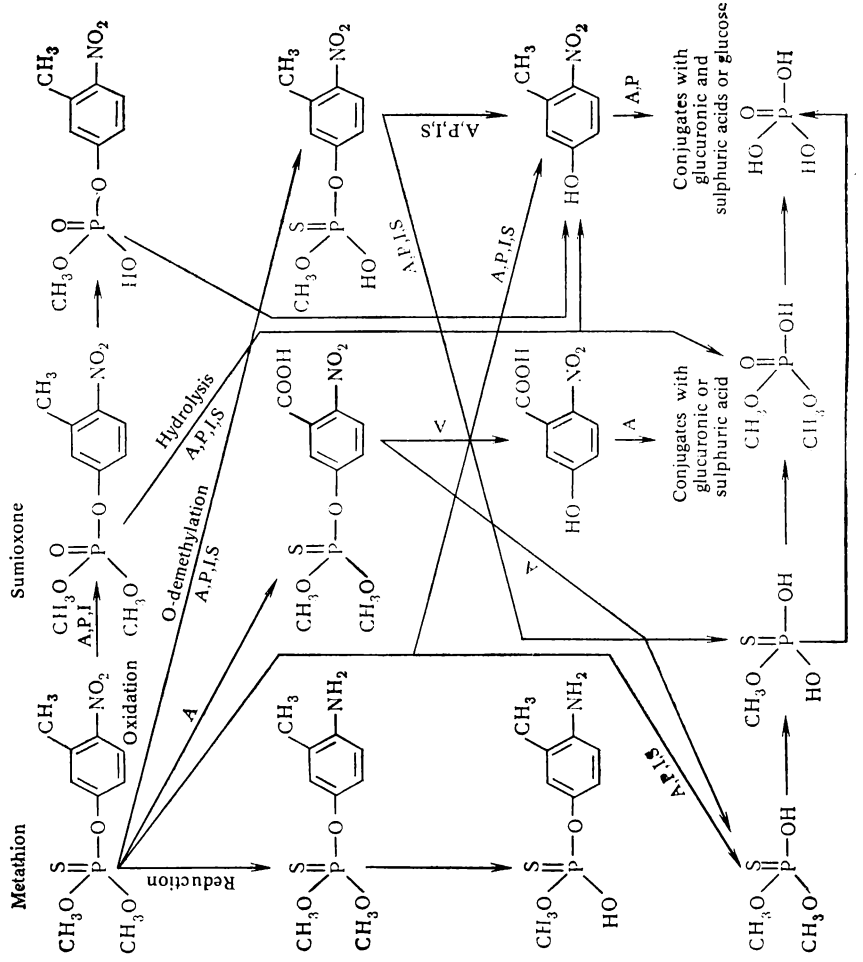


Fig. 9. Diagram of metabolism of fenitrothion (A = animal; I = insect; P = plant; S = soil)

onic and sulphuric acids or glucose; O-demethylation; and oxidation to the oxy analogue (sumioxon) with subsequent O-demethylation or hydrolysis along the P—X bond (see Fig. 9). The products of metabolism are involved in the general physiological processes of the plants or decompose into simple compounds such as CO_2 and NH_3. Residues of fenitrothion and its main metabolites are detected in 10-20 days after treatment.

In its recommended doses and concentrations, fenitrothion has no negative effect on cultural plants. Oil emulsifiable concentrates in damp weather may burn the leaves of wheat and alfalfa, especially with low-volume spraying. Burns also appear in some species of fruits and cabbage at a working solution concentration exceeding 0.2% and upon treatment in the initial period of development.

Fenitrothion is a contact insecticide and acaricide with a high initial toxicity and a short protective action. When it gets onto a plant, it partly penetrates into the tissues with the resultant penetration effect. The protective action exhibits itself not longer than 10 days after treatment, therefore it is recommended to use the substance with the addition of specific acaricides.

Fenitrothion is highly toxic to sucking pests (aphids, bugs, mites, psyllids), the larvae of *Lepidoptera*, especially moths, and *Diptera*.

Tests have also shown the high effectiveness of this insecticide in controlling barn pests and synanthropic insects.

It is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 516, and for mice is 715 mg/kg), and has a moderate chronic and dermal toxicity. When it enters an organism, the toxicant hydrolyses considerably more rapidly in the liver along the P—O bond than parathion-methyl.

The reactions of O-demethylation and oxidation to sumioxon, which rapidly hydrolyzes, proceed simultaneously (see Fig. 9). The products of these reactions have a low toxicity to animals and are excreted with the urine during one or two days after injection. This explains why fenitrothion has a lower toxicity to mammals than parathion-methyl.

In connection with the better toxicological properties of fenitrothion, it is being widely introduced into agriculture as a substitute for parathion-methyl. Fenitrothion is marketed in the form of a 50% emulsifiable concentrate. It is recommended for use on fruit crops (apples, pears, cherries, plums) to control aphids, psyllids, mites, mobile primary and secondary larvae of San Jose and mussel scale apple moth caterpillars, leaf miners, winter moths, codling and plum fruit moths, pseudocaterpillars of fruit sawflies, and cherry fruit flies in a concentration of 0.1-0.3%; on citrus and subtropical crops to control mites, citrus white flies, mobile primary and secondary larvae of citricola and Japanese wax scales and laurel leafhoppers in a concentration of 0.1-0.2%; on sugar and table beets to control

black bean aphids, flea beetles and leaf miners in a concentration of 0.2-0.4%; on tobacco to control aphids in a concentration of 0.2%; in empty storage premises to control granary weevils, confused flour beetles, flour mites, saw-toothed grain beetles, and brown khapra beetles in a concentration of 0.7%. The rate of use of the formulation on field crops is 0.6-1 kg (0.3-0.5 kg a.i.), on fruit (including citrus) and tea crops, 2-8 kg (0.6-2.4 kg a.i.) per hectare, in premises 0.9-1.2 g (0.4-0.6 g a.i.) per m^2 at a rate of use of the liquid of 0.2-0.3 litre/m^2.

Fenitrothion has shown its high effectiveness in controlling the larvae of pentatomids, corn weevils, and rustic shoulder-knot moths on grain crops. The rate of use of the formulation in this case is 2-2.5 kg (1-1.25 kg a.i.) per hectare at a rate of use of the solvent of 25-50 litre/ha (aerial spraying). Fenitrothion is used on sugar and table beets by spraying during the vegetation period to control moths, leaf miners, leaf aphids, and beet webworms. The rate of use is 0.6-1.2 kg (0.3-0.6 kg a.i.) per hectare.

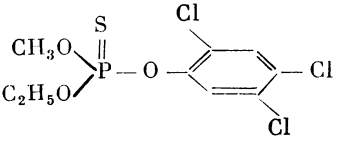
When controlling orchard pests, fenitrothion is used at rates of 1.6-4 kg (0.8-2 kg a.i.) per hectare. The use of fenitrothion with formulation No. 30 in a concentration of 0.1 + 1%, respectively, for controlling scale is also promising.

Owing to the high resistance of fenitrothion to hydrolysis, it can be used in combination with Bordeaux mixture, with preparation of the solution prior to use.

Treatment of fruit, field, and technical crops with formulations of fenitrothion must be discontinued 20 days before harvesting, and unfilled storage premises must be treated not later than in seven days before filling them. The harvest time for grain crops is 15 days. The tolerance level for fruits is 0.1 mg/kg.

Trichlorometafos-3

The active ingredient is O-methyl-O-ethyl-(2, 4, 5-trichlorophenyl) phosphorothioate:



The chemically pure substance is a light yellow liquid with an unpleasant odour boiling at 127 °C. Its volatility at 20 °C is 8 mg/m^3. It dissolves well in most organic solvents, while its solubility in water is under 40 mg/litre. In the chemical respect, trichlorometafos-3 is stable, especially in acid and neutral media; it does not hydrolyze in water even when boiled for 24 hours. In an alkaline medium,

hydrolysis occurs along the P=O bond with the formation of the products O-methyl-O-ethyl phosphoric acid and 2,4,5-trichlorophenol having a low toxicity.

Residues of the toxicant vanish from treated surfaces mainly because of evaporation and under the influence of meteorological factors. The persistence of the residues also depends on the specific features of the plants and ranges from 14 to 35 days.

In its recommended concentrations, trichlorometafos-3 does not cause burning of most plants. In early spring spraying, however, burns may appear on the foliage of apple, pear, and cherry trees. The sensitive plants also include cucumbers and peas.

Trichlorometafos-3 is a contact insecticide and acaricide with a high initial and a short protective and penetrating action. It can also function as a stomach poison. In its insecticidal properties, it is close to parathion-methyl, is a good killer of sucking pests and younger larvae of *Lepidoptera*, and is highly toxic to bees. In the form of an oil solution, trichlorometafos-3 exhibits a good ovicidal action and is effective in monitoring wintering stages of scales. The duration of the protective action of the toxicant averages 14 days.

Trichlorometafos-3 is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 567 mg/kg), and has moderate cumulative properties.

Application of the substance to the skin may produce hyperemia, edemas, and desquamation.

The comparatively low toxicity is explained by trichlorometafos-3 rapidly decomposing into only slightly poisonous substances in mammals' organisms. First of all, hydrolysis of the P—O (Alk) bond (demethylation) takes place, whereas in insects' organisms hydrolysis of the P—O bond occurs, to which trichlorometafos-3 is sufficiently stable. The hydrolysis products are rapidly detected in the urine of animals, the main one of them is O-ethyl-O-(2,4,5-trichlorophenyl) phosphorothioic acid.

In doses of 35-40 mg per kg of live mass, trichlorometafos-3 has no harmful effect on animals, is not deposited in the meat of fat and is not secreted with the milk. This explains the use of the toxicant to control exo- and endoparasites of horned cattle.

To monitor the pests of agricultural crops, a 50% emulsifiable concentrate of trichlorometafos-3 is used: on fruit crops to control various species of mites, bugs, aphids, psyllids, the caterpillars of apple moths and leaf miners, primary and secondary scale larvae, primary caterpillars of leaf roller moths, pierid butterflies and gypsy moths in a concentration of 0.1-0.2%; on grapevines to control the larvae of mealybugs and scale, primary and secondary caterpillars of European grape moths in a concentration of 0.2%; on sugar beets, tobacco, cucumbers, and tomatoes to control aphids, mites, and thrips; on cabbage to control cabbage aphids, the caterpillars of cab-

bage butterflies and moths in a concentration of 0.1-0.3%; on cherry and plum trees to control sucking pests and the larvae of cherry fruit flies and plum fruit moths in a concentration of 0.1-0.2%; on currants and gooseberries to control sawflies and midges in a concentration of 0.2%; on citrus and tea plantations to control a collection of sucking pests in a concentration of 0.1-0.2%. The rate of use on field crops is 1-2 kg (0.5-1 kg a.i.) per hectare, on fruit trees and berry plants is 1.2-4 kg (0.6-2 kg a.i.) per hectare, on citrus and tea plantations it is 4-8 kg (2-4 kg a.i.) per hectare.

The pesticide is also used to control stored-grain pests (the method of moist disinsection) at a rate of 0.5-2 g of the formulation and 0.2 litre of water per m^2, for impregnating catching bands (1.5% emulsion) placed on the trunks of apple trees to monitor codling moth caterpillars of the older ages, and on cotton—2 kg (1 kg a.i.) per hectare.

Trichlorometafos-3 is the basis for the preparation of trichlorol-5 (a substitute for DNOC and carbolineum) for the early spring treatment of fruit orchards. It includes 5% of trichlorometafos-3, 92% of nephitocidal petroleum oil, and 3% of an emulsifier. The substance readily penetrates through the shells of pests' eggs and the wax scales of scale insects and has a toxic action on the developing embryons of eggs and awakening larvae. Treatment should be performed not long before the larvae emerge from the eggs, but before opening of trees' buds to prevent burning of the young foliage. It is recommended to use trichlorol-5 on fruit plants before opening of the buds (the phenophase "bud swelling") to control the wintering stages of the San Jose, mussel and Japanese long scales, spider and gooseberry mites, apple moths, fruit-tree tortrix moths, rose leaf rollers, and common vapourer moths in a concentration of 2-3% and a rate of use of 25-50 kg (1.25-2.5 kg a.i.) per hectare. In its effectiveness, it is not inferior or is even superior to DNOC, and also formulations No. 30, 30a, 30c, and nitrafen. At the same time, trichlorol-5 is less toxic to humans than DNOC, and less phytocidal than all other pesticides. Burning of foliage and damaging of shoots are noted only when the spraying times are not observed.

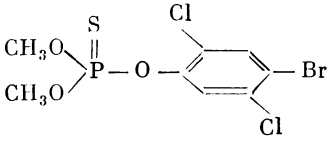
The spraying of orchards, cotton, sugar beets, citrus orchards, tobacco must be discontinued 30 days before harvesting; berry patches, cucumbers, and tomatoes—before blossoming; cabbage—before formation of the head; and grapevines—45 days before harvesting.

Granaries and the like are treated not later than 10 days before filling them.

The tolerance levels of trichlorometafos-3 in fruits and vegetables are 1, and in grain, 0.5 mg/kg.

Bromophos (Nexion)

The active ingredient is O,O-dimethyl-O-(4-bromo-2,5-dichlorophenyl) phosphorothioate:



In the pure form, it is a yellowish crystalline substance with a faint characteristic odour melting at 54 °C. Its solubility in water at 20 °C is about 40 mg/litre. It dissolves well in most organic solvents. The compound is thermally stable and has a low volatility, but it decomposes under the action of ultraviolet radiation.

Bromophos is stable in an acid medium, but readily hydrolyzes in alkaline conditions. At 22 °C and a pH of 13, 50% of the substance decomposes in 3.5 hours. It hydrolyzes in two directions: breaking of the P—O bond with the formation of O,O-dimethylphosphoric acid and 2,5-dichloro-4-bromophenol, and breaking of the P—O(Alk) bond with the formation of O-methyl-O-(2,5-dichloro-4-bromophenyl) phosphorothioic acid and methyl alcohol. The products formed are less stable and have a low toxicity to animals.

Bromophos rapidly decomposes on plants, especially during the first seven days, but its residues (not over 1 mg/kg) are also detected in 13-20 days after treatment. Upon penetrating into plants, it rapidly decomposes with the participation of phosphatases via the mechanism of double dealkylation with the formation of O-(2,5-dichloro-4-bromophenyl) phosphorothioic acid. This process is characteristic of bromophos and apparently occurs in mammals' organisms.

When properly used, bromophos does not burn the leaves of most cultural plants. In individual cases, the leaves of sweet cherry trees, alfalfa, and sugar beets were damaged. The toxicant does not change the organoleptic properties of agricultural products.

Bromophos is a contact insecticide with a low persistence (it protects plants during 7-13 days). It is highly effective for controlling aphids, fruit flies and their larvae, caterpillars of *Lepidoptera* and pseudocaterpillars of sawflies. It is moderately toxic to bees (they perish only on the first day after treatment).

Bromophos has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 3410 mg/kg), with weak cumulative properties. It has an irritating action on the skin and mucous membranes.

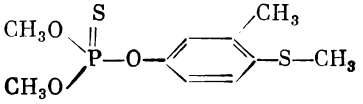
Bromophos is marketed in the form of a 25% and 40% emulsifiable concentrate and is recommended for use in fruit orchards to control cherry fruit flies, codling moths, leaf roller moths and aphids in a concentration of 0.1-0.2%; on berry patches to control common gooseberry sawflies and black currant leaf midges—0.05-0.2%; on cabbage to control leaf miner caterpillars—0.2-0.4%. The rate of use is 1-6 kg (0.4-1.5 kg a.i.) per hectare.

In tests, bromophos protected trees from cherry blackflies for seven days. Spraying of gooseberries with a 0.1% bromophos emulsion to control the third generation of sawflies exterminated 100% of their pseudocaterpillars.

Treatment of orchards, berry patches, and vegetable crops with bromophos must be terminated 15 days before harvesting the crop. The tolerance level in cabbage and fruits is 0.5 mg/kg, in berries it is 0.1 mg/kg.

Fenthion (Lebaycid, Baytex, Mercaptophos)

The active ingredient is O, O-dimethyl-O-{3-methyl-4-(methylthio) phenyl} phosphorothioate:



The pure substance is a colourless and almost odourless oily liquid boiling at 87 °C. It dissolves poorly in water (54-56 mg/litre at room temperature) and well in most organic solvents.

Fenthion is stable to hydrolysis and heating. At 80 °C, 50% of it hydrolyzes in an acid medium during 36 hours, and in an alkaline one during 95 minutes. When reacted with oxidizing agents, the substance is first oxidized to sulphoxide, and then to sulphone. Next the sulphone under the influence of the oxidizing agents detaches the thion sulphur and transforms into the relevant ester of phosphoric acid. All these oxidation products in their toxicity to animals are equal to fenthion or superior to it. This process may also occur on treated surfaces under the action of solar radiation and elevated temperatures.

In natural conditions, fenthion remains on porous surfaces (the walls of premises) several months. The decomposition process is more rapid on the surface and inside plants, but its residues are nevertheless detected in 14-21 days after treatment. In the first stages of metabolism of fenthion, no loss of toxicity occurs in plants because the sub-

stance is first oxidized to sulphoxide and sulphone, and also to O, O-dimethyl-O-{3-methyl-4-(methylthio)phenyl} phosphate, and regrouping to O-methyl-S-methyl-O-{3-methyl-4-(methylthio)phenyl} phosphorothioate occurs.

In the recommended concentrations, fenthion does not harm most species of agricultural plants. It persists for a long time in water (at a concentration of 2 mg/litre up to 105 days) and changes its taste and odour; this is why its residues are not tolerated in water basins.

Fenthion is a contact and stomach insecticide with a high initial toxicity and a prolonged protective effect (up to three weeks). Its acaricidal toxicity is slight. The substance controls almost 30 species of pests from various orders of insects, and is especially toxic to weevils, aphids, and stored-grain pests.

Fenthion is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 250 mg/kg) and has an acute chronic toxicity. When it is ingested into an animal's organism, it accumulates in the fat, muscles, and some internal organs, and is secreted with the milk. Fenthion is stable in food products. For example, the amount of its residue in milk does not change when the latter is stored in a refrigerator, pasteurized, boiled, or skimmed. This is why its tolerance levels in grain have been established equal to 0.15 mg/kg, and in meat, 0.2 mg/kg. No fenthion residues are tolerated in milk and in children's and dietary food products.

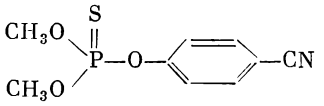
A 40% wettable powder of fenthion is recommended for use to control common and gray beet weevils on beet fields before the beginning of the mass emergence of the beetles from the soil at a rate of 4 kg/ha, and on sugar beet fields at a rate of 2.5-4 kg (1.0-1.6 kg a.i.) per hectare.

In tests, the extermination of beetles after using fenthion reached 98-100%. The insecticide is superior in its effectiveness to polychloropinene and toxaphene. The sufficiently high persistence of fenthion allows it to be used before the appearance of shoots, which prevents damage to the seed leaves of sugar beets.

A 50% emulsifiable concentrate of fenthion is used for the moist disinsection of seed grain storage bins and spraying storage premises and the territory adjoining them 10 days before the grain arrives for storage. At a concentration of the working solution of 0.2% and a rate of use of the insecticide of 0.6-1 g/m^2, fenthion ensures the complete eradication of beetles, grain and other weevils, and flour beetles during three days after treatment.

Cyanophos (Cyanox)

The active ingredient is O,O-dimethyl-O-(4-cyanophenyl) phosphorothioate:



The pure substance is a clear amber liquid (melting point = 14-15 °C). It dissolves well in alcohols, ketones, aromatic hydrocarbons, and poorly in water (46 mg/litre at 30 °C). In an alkaline medium, it rapidly decomposes along the ester bond to form products with a low toxicity.

It is not phytotoxic to agricultural plants in the recommended concentrations.

Cyanophos is a contact and a stomach insecticide having a broad spectrum of action with a prolonged protective effect (15-20 days). It is highly toxic to leaf beetle caterpillars, the larvae of leaf miners, mealybugs and scales, and also to aphids and weevils. It is distinguished for its high initial action and its penetrating effect.

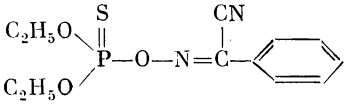
The insecticide is moderately toxic to humans and animals (LD_{50} for rats is 670 mg/kg), has a slight dermal toxicity (LD_{50} for dermal application is 1200 mg/kg), and moderate cumulative properties ($C_{cum} = 3.8$).

The pilot use of a 50% emulsifiable concentrate of cyanophos is allowed in apple orchards to control codling and Oriental moths, leafhoppers, leaf roller moths, leaf miners, aphids, mobile primary and secondary larvae of scales with a concentration of the working solution of 0.2% and at a rate of 2-5 kg (1-1.5 kg a.i.) per hectare; on grapevines to control leaf roller moths and mealybugs during the period of the mass hatching of larvae, and in citrus orchards to control white flies, the larvae of mealybugs and scales at a rate of 2-3 kg (1-1.5 kg a.i.) per hectare; on cabbage to control leaf caterpillars—1-1.2 kg (0.5-0.6 kg a.i.) per hectare; on sugar beets to control weevils, leaf miners, and leaf aphids—1-3 kg (0.5-1.5 kg a.i.) per hectare. In tests on sugar beets, cyanophos was superior to polychloropinene in its toxic effect and rate of action.

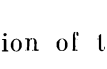
The harvest time of this insecticide for all crops is 20 days.

Phoxim (Volaton, Baythion, Valexon)

The active ingredient is O,O-diethyl phenylglyoxylonitrile phosphorothioate:



In the pure form, it is a yellowish liquid without a characteristic odour,* virtually non-volatile, poorly soluble in water (7 mg/litre at 20 °C) and well soluble in organic solvents.

It is easily decomposed by alkalies into non-toxic products. It is unstable on treated surfaces, and under the influence of ultraviolet radiation isomerizes with the formation of the isomer  . Small amounts of tetraethyl pyrophosphate and its monothio analogue are also formed (these are highly toxic substances). The action of ultraviolet radiation leads to an increase in the toxicity of the substance, but its persistence diminishes owing to the appearance of substances unstable to hydrolysis. Such a reaction may also proceed on treated plants. When a granulated formulation is incorporated into the soil, its residues are detected during three or four months.

In its recommended rates of use, phoxim does not harm plants. When the concentration or the rate of use is increased, however, suppression of the growth and lowering of the yield of some crops are noted.

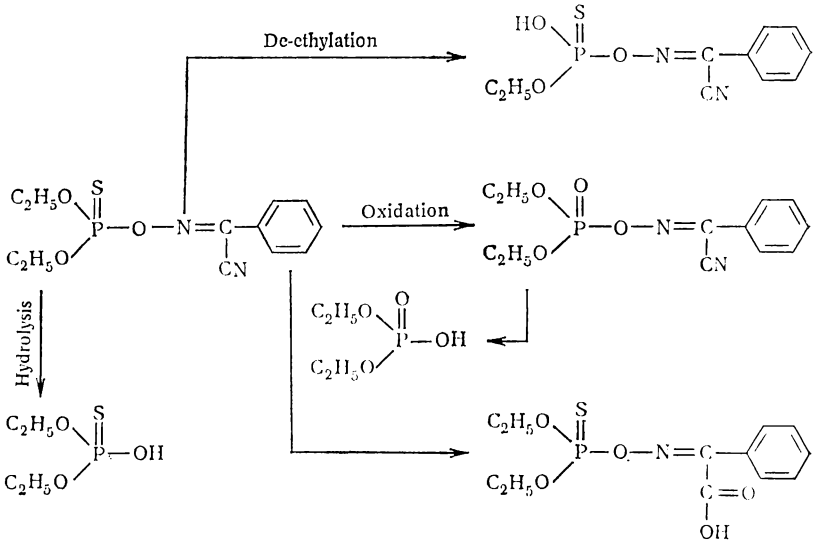
The toxicant rapidly decomposes in plants. In one day after treatment of cotton, about 20% of the initial amount is discovered, and in five days, only 1%.

Phoxim is a contact and stomach insecticide with a high initial toxicity, a broad spectrum of action and a brief protective effect. It is highly toxic to *Orthoptera*, beetles, *Lepidoptera* and their larvae, aphids and stored-grain pests. The period of protective action is three to five days. In preliminary tests, it was found promising for controlling wireworms and false wireworms, ensuring a reduction of 90-95% in their population on corn and an increase in the harvest of 2-2.5 times on the background of a large population (over 30 larvae per m^2), and also for protecting vegetable crops and potatoes from leaf pests.

When a granulated formulation is incorporated into the soil, it persists for 25-30 days.

Phoxim has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 1750 mg/kg) and moderate cumulative properties (LD_{50} for rats applied dermally is 1000 mg/kg). In mammals' organisms, it rapidly metabolizes in the following directions: the forma-

tion of oxone with its rapid hydrolysis to diethylphosphate; hydrolytic breaking of the ester bond P—X; hydrolytic transformation of the nitrile group into a carboxyl one, and de-ethylation:



The high selective toxicity of the insecticide is explained by the specific property of the oxone of phoxim to inhibit the acetylcholinesterase of insects 270 times stronger than that of the erythrocytes of the blood, and by the rapid metabolism of the insecticide in mammals' organisms to non-toxic products (the accumulation of phoxim and its oxime is noted in insects' organisms).

A 50% emulsifiable concentrate and 5% granulated phoxim are used to monitor pests of plants.

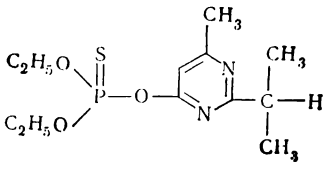
The emulsifiable concentrate is recommended for controlling the Colorado beetle on potatoes, leaf caterpillars on cabbage at a rate of 1-1.5 kg (0.5-0.75 kg a.i.) per hectare, and for pilot use on winter wheat for controlling cereal leaf beetles (spraying of the shoots) at a rate of 2 kg (1 kg a.i.) per hectare.

The 5% granulated formulation is incorporated into the soil when sowing together with the seeds of corn for controlling wireworms (the South of the European part of the USSR) at a rate of 50 kg (2.5 kg a.i.) per hectare. It is permitted to be used on winter wheat by incorporation into the soil when sowing to control cereal leaf beetles—75 kg (3.75 kg a.i.) per hectare.

The harvest time when using the emulsifiable concentrate is 20 days.

Diazinon (Basudin)

The active ingredient is O-O-diethyl-O-(2-isopropyl-4-methyl-6-pyrimidinyl) phosphorothioate:



In the pure state, it is a colourless oily liquid boiling at 89 °C. It is poorly soluble in water (40 mg/litre at room temperature) and well soluble in most organic solvents. Its volatility at 20 °C is 1.39 mg/m^3.

Diazinon is relatively easily hydrolyzed in an alkaline and acid media. In alkaline conditions, diethylphosphoric acid and 2-isopropyl-4-methyl-6-oxypyrimidine are formed, and in acid conditions, in addition to these substances, a small amount of tetraethyl phosphorodithioates and pyrophosphorothioates.

Residues of diazinon in the soil (0.1 mg/kg) are detected in 12-14 weeks after the introduction of the granulated formulation. But 50% of the substance decomposes in only two or three weeks. In addition to physical and chemical factors, microorganisms in the soil play an active role in this process.

Diazinon introduced into the soil is absorbed very well by the roots of plants and moves into the green organs, accumulating here in insecticidal amounts. This is why the toxicant protects the shoots of crops from pests during 7-15 days. No residues of the insecticide are discovered in the crop. When vegetating plants are treated, diazinon is discovered in their leaves only during the first 7-10 days.

Diazinon decomposes in plants in two directions: (1) oxidation of the phosphorothioate to the corresponding phosphate (diazoxone) followed by hydrolysis of the P—X bond with the formation of nontoxic diethylphosphoric acid and 2-isopropyl-4-methyl-6-oxypyrimidine, and (2) the oxidation of the side isopropyl group of the ring with the subsequent hydrolysis of the P—X bond with decomposition of the heterocyclic ring and the liberation of CO_2.

In its recommended doses, diazinon exhibits no phytocidal properties. When seeds and the roots of seedlings are treated with a diazinon solution, inhibition of the growth of the root system and shoot is noted. Lettuce belongs to the sensitive cultures.

Diazinon is a contact and systemic insecticide with a brief persistence. It is highly toxic to the larvae of *Diptera*, the imagoes and larvae of beetles, especially weevils, various species of aphids and cutworms. The duration of the protective action in spraying plants is 7-14 days. The perennial use of diazinon is attended by the appearance of insects resisting organophosphorus compounds. The acquired resistance is explained by the lower penetrability of the integuments of the insects and the higher activity of the enzymes in their organisms. A feature of the enzyme systems of resistant insects is their ability to oxidize the 4-methyl group of diazinon's heterocyclic ring to the 4-COOH radical, which leads to the loss of toxicity and facilitates the further decomposition of the substance.

Diazinon relates to substances that are highly toxic to humans and animals (LD_{50} for laboratory animals is 76-130 mg/kg). It penetrates through the skin, and has a slight chronic toxicity.

A 40% wettable powder of diazinon is recommended for treating plantings of sugar beets against aphids, weevils, and flea beetles at a rate of use of the insecticide of 2.5 kg (1 kg a.i.) per hectare, and of wheat against cereal leaf beetles at a rate of 2-2.5 kg (0.8-1 kg a.i.) per hectare.

A 60% emulsifiable concentrate of diazinon is used for controlling leaf aphids on seed and industrial plantations of sugar beets at a rate of 0.8 kg of the formulation (0.5 kg a.i.) per hectare; weevils and other pests on seed plantations of alfalfa at a rate of 2-3 kg (1.2-1.8 kg a.i.) per hectare in the stage of budding and fruit formation, and cereal leaf beetles on wheat at a rate of 1.5-1.8 kg (0.9-1.1 kg a.i.) per hectare.

A 10% granulated formulation at a rate of use of 40-50 kg (4-5 kg a.i.) per hectare is incorporated into the soil in the period of growth of alfalfa to control a group of pests; it is recommended for pilot use on sugar beets to control cutworms without embedding in the soil, for incorporation together with corn seeds when sowing in the conditions of the South of the European part of the USSR to control wireworms at a rate of 40-50 kg (4-5 kg a.i.) per hectare.

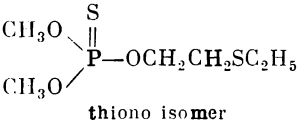
A 5% granulated formulation is incorporated into the soil together with the seeds of winter wheat to control the larvae of cereal leaf beetles at a rate of 50 kg (2.5 kg a.i.) per hectare, and together with corn seeds to control click beetles in the same way as the 10% formulation at the same rate of use.

The harvest time for wheat is 30 days and for sugar beets, 20 days. The harvest time for the 10% granulated formulation for sugar beets is 30 days.

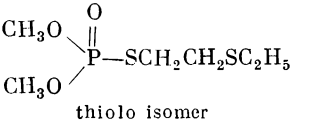
The tolerance levels of basudin in cabbage, onions, and potatoes is 0.1, in grain is 1.0, and in tomatoes, beets, and cucumbers 0.5 mg/kg.

Demeton Methyl (Metasystox, Metilmercaptofos)

The active ingredient is O,O-dimethyl-O (or S)-{2(ethylthio)ethyl} phosphorothioate (or O,O-dimethyl-2-ethylmercaptoethyl phosphorothioate). It has two isomers:

I. 

thiono isomer

II. 

thiolo isomer

Both isomers have insecticidal properties, and this is why they are not separated thoroughly when produced. The technical product contains 70% of the thiono and 30% of the thiolo isomer.

The chemically pure isomers of demeton methyl are yellowish oily liquids with an unpleasant odour well soluble in organic solvents. The solubility in water of the thiono isomer is 330 mg, and of the thiolo one, 3300 mg/litre, their volatility is 23.3 and 4.5 mg/m^3, respectively.

Both isomers rapidly decompose in an alkaline, and the thiolo one, in an acidic medium. In storage of the insecticide, regrouping of the thiono isomer into the thiolo one occurs. This process accelerates in the presence of water. In these conditions, demeton methyl enters into a reaction of intermolecular methylation, which is sometimes the cause of spoilage of the product in prolonged storage.

Under the action of oxidizing agents, the isomers of demeton methyl become oxidized to the relevant sulphoxides and sulphones, with no losses of anticholinesterase activity and toxicity.

The substance rapidly decomposes on treated surfaces in natural conditions into non-toxic products, but in the tissues of some plants (eggplants) it may persist up to two months.

Demeton methyl is rapidly absorbed by the roots and leaves of plants, moves quite well along the xylem or phloem, and accumulates temporarily in the cells. It may be excreted from plants through the stoma in the form of drops or a vapour. On the surface of and inside a plant, demeton methyl undergoes various transformations under the action of enzymes.

The metabolism of the insecticide follows two paths: oxidation of the sulphur with the formation consecutively of P-sulphoxide, P-sulphone, and P-sulphone, and regrouping into the thiolo isomer with the following oxidation of the ester sulphur and the formation of the relevant sulphoxide and sulphone. As a result of these transformations, substances are formed that are not inferior and are even

superior to the initial product in their toxicity and persistence. Only the subsequent hydrolysis to O,O-dimethyl phosphoric acid leads to the loss of toxicity.

In its recommended concentrations, demeton methyl has no negative effect on the plants being protected.

Demeton methyl is a contact and systemic insecticide with a high initial toxicity and a prolonged protective effect; its action continues up to 20-25 days. It is highly toxic to pests with sucking mouth parts. It is less dangerous to beneficial insects and predatory mites than other insecticides owing to its rapid penetration into plants.

Upon the regular use of this insecticide, insects, especially mites, develop a specific resistance to organophosphorus compounds.

The technical product is highly toxic to humans and warm-blooded animals (LD_{50} for rats is 80-100 mg/kg) and has an acute dermal and chronic toxicity. It also results in poisoning when it enters through the respiratory tracts (the threshold concentration is 0.1-0.2 mg/m^3).

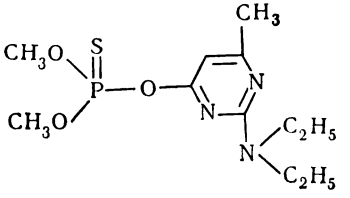
Owing to its unfavourable toxicological properties, it is to be replaced.

A 30% emulsifiable concentrate of demeton methyl is used on hops and cotton to control mites, aphids, and thrips at a rate of use of the insecticide of 1.5-2 kg (0.45-0.6 kg a.i.) per hectare; on sugar beets, including seed plantations, to control aphids at a rate of 0.8-1 kg (0.2-0.3 kg a.i.) per hectare. A great merit of this insecticide is the duration of its protective action, which makes it possible to reduce the number of treatments a season. Demeton methyl may be used on cotton, however, only in regions where mites have not developed resistance to organophosphorus compounds. The harvest time for sugar beets is 45 days, and for hops and cotton, 20 days.

The tolerance level of demeton methyl in apples, sugar beets, and hops is 0.7 mg/kg.

Pirimiphos-Methyl (Actellic)

The active ingredient is O,O-dimethyl-O-(2-diethylamino-6-methyl-pyrimidin-4-yl) phosphorothioate:



In the pure form it is a straw-coloured liquid with a low volatility. It dissolves well in organic solvents (benzene, chloroform, ethyl

alcohol) and poorly in water (5 mg/litre at 30 °C). It is chemically stable, but in an alkaline and strongly acidic media decomposes into non-toxic products.

It persists from 11 to 15 weeks on the treated surfaces of residential or storage premises. The main losses of the substance from a treated surface are due to evaporation.

In water, pirimiphos-methyl retains its toxicity from 6 to 11 weeks, vanishing from this medium as a result of evaporation and photolysis. In the soil, the substance migrates poorly, its half-life in various soils fluctuating within four weeks.

In the recommended rates of use, it has no negative effect on the plants being protected and does not change the organoleptic properties of products. After the treatment of plants, it rapidly (in two or three days) vanishes from their surface because of evaporation.

Pirimiphos-methyl is a contact insecticide and acaricide with fumigational and penetrating action. It is highly toxic to sucking (aphids, bugs, mites, scale insects, mealybugs, and thrips) and mandibulate (beetles and their larvae, caterpillars of *Lepidoptera*) pests. The period of protective action is 10-15 days.

The insecticide has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 2050 mg/kg), and its dermal toxicity is only slight. According to the results obtained by the firm producing it (ICI of Great Britain), pirimiphos-methyl has no remote negative effects.

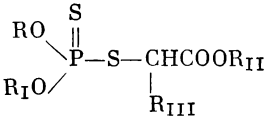
In the USSR, a 50% emulsifiable concentrate of pirimiphos-methyl is permitted to be used for pilot applications on cucumbers, tomatoes, peppers, eggplants, and ornamentals at a rate of 3-6 kg of the formulation (1.5-3 kg a.i.) per hectare in sheltered soil and 0.3-1.5 kg (0.15-0.7 kg a.i.) per hectare in open soil to control a set of pests; on raspberries and strawberries to control aphids and leaf-eating pests, on gooseberries to control leaf roller moths, gooseberry fruit worms, sawflies, and aphids; on grapevines to control leaf roller moths, vine lice, and mealybugs at a rate of 0.6-3 kg (0.3-1.5 kg a.i.) per hectare, and also for treating empty storage premises at a rate of 0.5 g (0.25 g a.i.) per m^2.

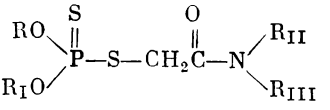
The last treatment of vegetable and decorative plant crops in sheltered soil with pirimiphos-methyl may be performed three days prior to harvesting with obligatory washing of the products with water, and of vegetables in open soil, berry patches, and grapevines, 20 days prior to harvesting.

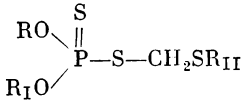
8. Phosphorodithioic Acid Derivatives

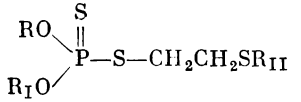
These compounds in the majority of cases are considerably less toxic to mammals and more stable chemically than the corresponding derivatives of phosphorothioic acid. The pesticides of this group

include stomach-contact insecticides and systemic insecticides and acaricides that make it possible to lower the harm to the beneficial insects. Compounds with the following general formulas are in the greatest favour:

I. 

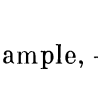
II. 

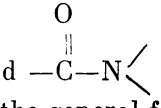
III. 

IV. 

Among these substances, those in which R and R_I are methyl radicals are the least toxic to humans.

In the series of compounds of the general formula I, substances in which R_{II} is an aliphatic and R_{III} is an aromatic radical have the highest activity.

At the same time, when a carboxyl group (for example, ) is introduced into the aliphatic radical R_{III}, the toxicity of the substance to vertebrates sharply drops, but this does not virtually affect its insecticidal and acaricidal properties.

Compounds of the general formula II are not only contact, but also systemic insecticides. In the amide group, R_{II} is a lower aliphatic radical, generally CH_3, while R_{III} is hydrogen or a radical. An increase in the number of carbon atoms in R_{II} to above two and the substitution of a hydrocarbon radical for hydrogen lead to diminishing of the insecticidal activity of the substance. The toxicity of compounds of the general formula II to humans and animals is substantially lower than to insects, which is explained by the active breaking of the bond  under the influence of amidases.

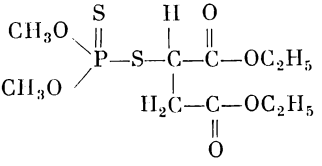
In compounds of the general formulas III and IV, R_{II} is an aliphatic or an aromatic radical. In substances of formula III, the substitution of an aromatic radical for R_{II} leads to lowering of the toxicity to mammals with retaining of the insecticidal and acaricidal properties.

Compounds of the general formula IV in which R_{II} is a lower aliphatic radical are distinguished by their prolonged systemic action and high toxicity to humans and warm-blooded animals.

In addition to the described groups of substances, compounds with various substituents in the anhydride part X of the molecule, including heterocycles, have been separated among the derivatives of phosphorodithioic acid, but a clear-cut relation between their insecticidal activity and structure has not been established to date.

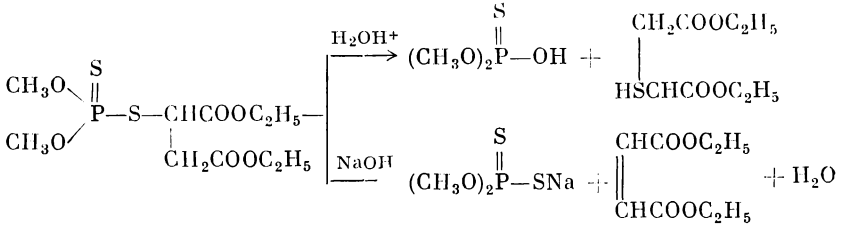
Malathion (Carbofos)

The active ingredient is O,O-dimethyl-S-(1,2-dicarbethoxyethyl) phosphorodithioate:



The pure substance is a clear to amber liquid boiling at 120 °C and solidifying at 2.85 °C. Its volatility is 2.26 mg/m³. It dissolves well in organic solvents, except for saturated hydrocarbons. Its solubility in water at 20 °C is 145 mg/litre.

Malathion has a low thermal stability, and upon elevation of the temperature it intensively decomposes with the formation first of the more toxic thiolo isomer. The substance hydrolyzes in acidic and alkaline media:



The compounds formed have a low toxicity to living organisms. Oxidizing agents cause malathion to transform into the corresponding P=O analogue (malaoxon) having a high physiological activity. The same process occurs in the organism of an insect and to a smaller extent is a feature of plants and mammals.

Upon prolonged contact with iron, the insecticide decomposes and completely loses its toxic properties. This is why it must never be stored in iron containers.

Malathion rapidly vanishes from the surface of treated plants because of chemical and enzymatic decomposition and evaporation. In plants' tissues, it is intensively hydrolyzed by phosphatases and

carboxyesterases along the bond P—X and —C(=O)—OR to form dimethyl phosphorothioic acid, and other acids having a low toxicity. The residues of malathion in field conditions vanish in 10-15 days, and in sheltered soil, in 7-8 days after treatment.

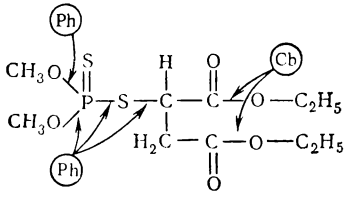
In its recommended doses and when properly used, malathion does not harm the plants being protected. Slight burns were observed on some species of peaches, apricots, sweet cherries, and on greenhouse crops.

Malathion is a contact insecticide and acaricide with a high initial toxicity and a brief protecting and penetrating action. Its persistence in field conditions is up to 10 days, and in conditions of sheltered soil, 5-7 days.

The high toxicity of malathion to pests is due to its transformation into the more toxic malaoxon in an insect's organism, while the processes of hydrolysis of malathion occur much more slowly. Upon the perennial use of malathion, populations of insects and mites appear that are resistant to it or other organophosphorus compounds. The resistant individuals are distinguished by their great ability to decompose malathion into non-toxic products. This is due either to the appearance of the specific enzyme malathionoxidase, or to an increase in the activity of aliesterase and phosphatases. In the first case, specific resistance is produced only to malathion, in the second, to the entire group of organophosphorus compounds.

Malathion is effective mainly in controlling sucking insects and phytophagous mites, and also small caterpillars and the larvae of sawflies. It is highly toxic to houseflies, mosquitoes, and bees. When it gets into water basins, the pesticide kills many representatives of the zooplankton, for example, water fleas.

Malathion is moderately toxic to humans and warm-blooded animals, its toxicity depending on the purity of the substance. For the technical product, LD_{50} for rats ranges from 450 to 1300 mg/kg, and for the chemically pure substance, from 1000 to 2800 mg/kg. It has virtually no chronic toxicity and a low dermal toxicity. The comparatively low toxicity of malathion to mammals is explained by the features of its metabolism: (The points of decomposition of malathi-



on in a mammal's organism are shown in the diagram by the symbols Ph and Cb in circles, which stand for phosphatases and carboxyesterases, respectively.)

In a warm-blooded animal's organism, owing to the high activity of the carboxyesterases, the malathion molecules are decomposed first of all in the direction of hydrolysis of the $-C\begin{matrix}O\\ \diagup\\ \diagdown\\ O-\end{matrix}$ groups. The products are water-soluble malathion mono- and dicarboxylic acids that are easily excreted from the organism. Simultaneously, the phosphatases cause the other part of the molecule to decompose hydrolytically also with the formation of water-soluble products having a low toxicity. It must be noted that water-soluble and ionized substances do not virtually penetrate into the nervous system of an animal, but are easily excreted from the organism with the urine. A very small amount of malaoxon is formed in a mammal's organism.

A major advantage of malathion is that it does not accumulate in an animal's tissues. This explains its use by veterinarians to control exo- and endoparasites of animals and birds and to exterminate houseflies and mosquitoes in livestock barns.

The industry markets 30% and 50% emulsifiable concentrates. They are recommended for use on fruit and berry crops and on grapevines to control psyllids, aphids, mites, younger larvae of mealybugs, scale, moths, and other *Lepidoptera* in a concentration of 0.2-0.3% at a rate of 0.5-1.5 kg/ha; on cereals, corn, leguminous crops, flax, cotton, sugar and table beets, cabbage, tomatoes, cucumbers, sunflowers and other oil crops to control sucking pests at a rate of 0.1-0.2 kg (0.3-0.6 kg a.i.) per hectare; on seed plants of alfalfa, clover, and sainfoin against aphids at a rate of 0.1-0.3 kg a.i./ha; on tobacco against aphids and mites—0.5-0.9 kg/ha; on hop—0.9-3 kg; on citrus fruits and tea to control a collection of sucking pests at a rate of 1.8-2.4 kg; on melon crops—0.2-1.2 kg; on cucumbers and tomatoes in sheltered soil in a concentration of the formulation of 0.05-15% at a rate of 1.2-1.8 kg a.i./ha; in granaries to treat fodder and bread grain at a rate of 6-15 g/tonne.

For pilot application to control locusts, a 30% emulsifiable concentrate of malathion is recommended at a rate of use of 1.2-4.5 kg (0.4-1.3 kg a.i.) per hectare, and a 40% solution for ultrasmall volume spraying at a rate of 1.5 litres (0.6 kg a.i.) per hectare.

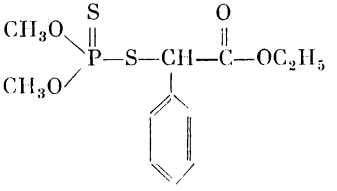
Malathion is appreciably inferior to other insecticides in controlling leaf-eating insects because it acts for a short time and only on the younger larvae.

Owing to its low toxicity to humans, malathion is permitted to be used in collective and individual gardens. The last treatment on all cultures may be performed 20 days before harvesting, on tobacco—seven days, while cucumbers in hotbeds and greenhouses may be

sprayed two days before harvesting provided that the vegetables are thoroughly washed when harvested. The tolerance level of the insecticide in grain is 3 mg/kg, and in vegetables, fruits, and other products—1 mg/kg. It is prohibited to treat berry patches in the fruiting season and tea-shrub plantations when the leaves are being gathered.

Phenthoate (Cidial, Elsan, Papthion, Dimethenthoate)

The active ingredient is O,O-dimethyl-S-(alpha-ethoxycarbonylbenzyl)phosphorodithioate:



It is a reddish yellow oily liquid with an aromatic odour, well soluble in most organic solvents and virtually insoluble in water (200 mg/litre).

At a temperature above 120 °C, phenthoate decomposes, but in ordinary conditions it is thermally stable. In an alkaline medium, it hydrolyzes with a loss of toxicity, but its resistance to hydrolysis is higher than in malathion. Its half-life in water at a pH of 7.6 and a temperature of 18-20 °C is 20 days. When the phenthoate content in water is 0.15-0.5 mg/litre, an unpleasant astringent taste appears.

When it gets onto plants, phenthoate penetrates very slightly into the tissues of leaves and fruits. It persists on plants from 20 to 25 days, and in the rind of citrus fruits up to 2.5 months. It affects the organoleptic properties of fruits already at a content in them over 0.1 mg/kg, and of tangerines even less than this amount.

Phenthoate does not harm plants in its recommended doses.

It is an insecticide and acaricide with stomach and contact action having a high initial toxicity and a prolonged protective effect (up to 20 days). It is highly toxic to sucking pests (mites, aphids, psyllids, scale insects and mealybugs) and mandibulate insects (the larvae of codling moths, leaf roller moths, etc.), and also to bees and entomophags. It is a repellent to some insects.

Phenthoate is highly toxic to humans and warm-blooded animals (LD_{50} for rats is 172 mg/kg) and has a slight dermal and cumulative toxicity. In a chronic test, no accumulation of the toxicant occurred in animals' organisms, but functional cumulation was noted.

A 50% emulsifiable concentrate of phenthoate is used to control pests. It is recommended for use on fruit crops against codling, plum,

and peach fruit moths, mobile primary larvae of San Jose and other species of scales; on grapevines against vine foresters, European grape moths, and mealybug larvae in a concentration of 0.2%. It simultaneously kills psyllids, aphids, mites, and larvae of leaf roller and fall web-worm moths. Phenthoate is superior to other insecticides in its effectiveness in controlling a variety of scales and mealybugs in the period of the mass appearance of mobile primary larvae. The extermination of the larvae remains at a level of 100% during 20 days after treatment. The rate of use of the substance is 2-6 kg (1-3 kg a.i.) per hectare.

When phenthoate is used in production conditions, contamination of the air occurs, and traces of the insecticide are noted during three days after treatment.

Phenthoate's odour is very persistent and remains in the air of treated sections up to 10 days.

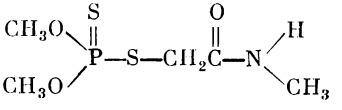
The shortcomings of phenthoate include its relatively high cost, but in the southern regions of industrial horticulture and viniculture the use of this insecticide against codling moths, scale insects and mealybugs ensured a high economical effect.

Fruit crops and grapevines may be sprayed with phenthoate not later than 30 days before harvesting. The treatment of citrus fruits is prohibited owing to the persistence of the insecticide's residues in the fruits and to the change in their organoleptic properties.

The tolerance level of phenthoate in fruits is 0.1 mg/kg.

Dimethoate (Fosfamid, Rogor, Perfekthion)

The active ingredient is O,O-dimethyl-S-(N-methylcarbamoylmethyl)phosphorodithioate:



In the pure form, it is a white crystalline substance with a camphor-like odour melting at 51-52 °C. It is well soluble in water (25 g/litre at 21 °C) and organic solvents except saturated hydrocarbons.

Dimethoate is thermally unstable and when heated decomposes after preliminary isomerization to the P=O analogue. The decomposition is appreciably accelerated by ultraviolet radiation.

In an aqueous medium, the substance hydrolyzes, the rate of hydrolysis increasing with a growing pH of the solution. This is attended by breaking of the bonds P—X and C(=O)—N— with the formation of

the only slightly toxic dimethyl phosphorothioic and dimethoate carboxylic acids, respectively. Dimethoate is relatively unstable in storage and rapidly loses its toxicity.

Dimethoate rapidly decomposes on the surface of a plant under the action of ultraviolet radiation, temperature, and water, but it retains its toxic properties within a plant up to 20 days. It penetrates very well into a plant through its leaves and roots, exhibiting a systemic action. Inside a plant, it moves well along the xylem (from the roots into the green part), but its movement along the phloem encounters obstacles, therefore virtually the entire dimethoate applied to a leaf remains in it.

The insecticide decomposes slowly in vegetative tissues. Three processes occur simultaneously, namely, hydrolysis of the P—X bond, O-demethylation with the formation of products having a low toxicity, and oxidation to the P=O analogue of dimethoate, a more powerful inhibitor of cholinesterase, which explains the insecticide's persistence (see Fig. 10).

Dimethoate does not damage plants when used properly and with strict observance of the doses. Burning of leaves is observed after the treatment of some species of peaches and apricots, chrysanthema, ornamental plants, hops, and of cultures in sheltered soil. It has a strong phytocidal action in increased concentrations.

Dimethoate is an insecticide and acaricide with a high initial contact toxicity and a short systemic action. Its protective effect lasts 15-20 days. It is highly toxic to sucking and mining pests (aphids, mites, psyllids, scale insects, and mealybugs), and to a smaller extent to mandibulate insects. Owing to its rapid penetration into a plant and decomposition on its surface, the toxic action of the insecticide on beneficial insects and predatory mites is short.

Dimethoate metabolizes in the organisms of insects and mites in the same way as in plants. Of great significance is the process of formation of the more toxic P=O-dimethoate.

Dimethoate is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 230 mg/kg), has weak chronic and acute dermal toxicity. Its toxicity to mammals is 1/325 of that to insects. The explanation is the differences in the metabolism of the insecticide. In a mammal's organism, owing to the high activity of the amidases, hydrolysis of dimethoate predominates with the formation of water-soluble and only slightly toxic dimethoatecarboxylic acid.

A 40% emulsifiable concentrate of dimethoate is used in agriculture. A 0.1% concentration is recommended for use on cotton to control red spider mites, aphids, and thrips at a rate of use of the formulation of 1.5-2.5 kg (0.6-1.0 kg a.i.) per hectare; on leguminous plants, flax, cabbage, alfalfa and vegetable seed plantings to control aphids and thrips; on sugar and table beets to control aphids, leaf miners, bugs, leafhoppers, and leaf beetles at a rate of 0.5-1 kg

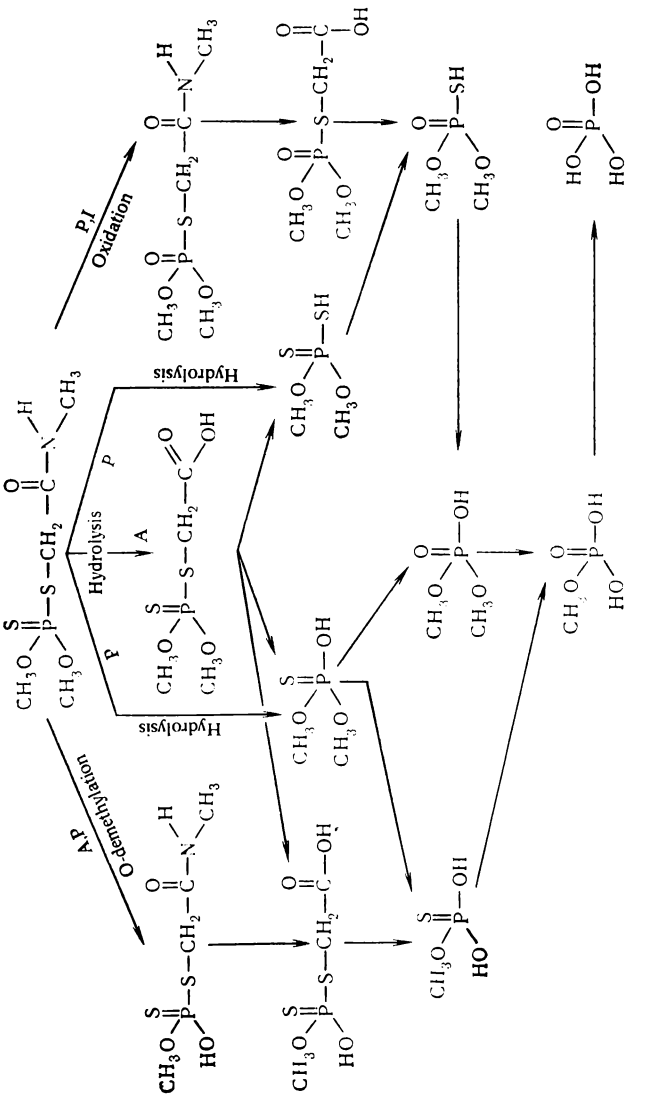


Fig. 10. Diagram of metabolism of dimethoate (A = animal; I = insect; P = plant)

(0.2-0.4 kg a.i.) per hectare; on cereal crops tomatoes, and melons to control aphids at a rate of 0.7-1.5 kg (0.3-0.6 kg a.i.) per hectare; on seed plantings of potatoes at a rate of 2-2.5 kg (0.8-1 kg a.i.) per hectare; on cucumber seedlings at a rate of 2-6 kg (0.8-2.4 kg a.i.) per hectare; on olive and mulberry trees at a rate of 2-3 kg (0.8-1.2 kg a.i.) per hectare; on tobacco to control aphids at a rate of 0.8-1 kg (0.3-0.4 kg a.i.) per hectare; on fruit (including citrus) trees and hops to control aphids, mites, psyllids, bugs, citrus whiteflies, the younger larvae of sawflies, leaf roller moths, apple worms and moths, scales, and mealybugs at a concentration of 0.1-0.2%; on grapevines to control red spider mites, the larvae of mealybugs, and scales at a concentration of 0.15-0.20%. The rate of use of the formulation is 0.8-6 kg (0.3-2.4 kg a.i.) per hectare.

A high effectiveness of dimethoate was obtained in the north-western zone of the USSR when used against pests of fruit crops in the early spring. With one application of the substance in the rose bud stage, the population of apple suckers decreased by 96-98%, of red fruit-tree spider mite—by 98-100%, of the caterpillars of winter moths and leaf roller moths—by 90-92%. The protective action of dimethoate against green apple aphids persists 45 days, against red fruit-tree spider mites—90-110 days. The persistence of dimethoate in treatment in the rose bud stage for most pests is over 14 days, which allows their control to be limited to one treatment. In this connection, dimethoate has been recommended in the north-western zone of the USSR to protect orchards from a group of pests. The rate of use of the formulation for early spring treatment in the rose bud stage is 1.5-2 kg (0.6-0.8 kg a.i.) per hectare with a concentration of 0.15-0.2%. An emulsifiable concentrate of dimethoate is also used to control sucking pests of hemp at a rate of 1.2-2 kg (0.48-0.8 kg a.i.) per hectare.

In addition to the emulsifiable concentrate of dimethoate, granulated formulations are also recommended, namely, 1.6% granulated dimethoate on superphosphate and granulated fosfaman (1.6% dimethoate + 1% lindane on superphosphate). They are used to control beet pests on sugar beets by incorporation with the seeds into the rows at a rate of 100-150 kg/ha of the formulation. Both formulations ensure a high initial toxic effect in controlling gray and common beet weevils and protect the shoots from damage during 25-28 days. Extermination of the pests reaches 90.6-95.9%. No residues of dimethoate are detected in plants on the 25th day after the emergence of shoots.

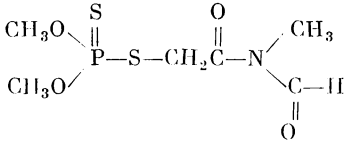
Granulated dimethoate is also used on alfalfa simultaneously with sowing and up to the beginning of emergence to control weevils at a rate of 50 kg (0.8 kg a.i.) per hectare; on fodder crucifers to control fleas at a rate of 20 kg (0.3 kg a.i.) per hectare; granulated dimethoate and fosfaman are used on oil-bearing poppies to control

gall weevils in the rows over the surface of the shoots at a rate of 50-70 kg (0.8-1.2 kg a.i.) and 70 kg (1.82 kg a.i.) per hectare, respectively, and fosfaman together with the seeds is used at a rate of 15-30 kg (0.39-0.78 kg a.i.) per hectare.

It is prohibited to use dimethoate on berry patches, and also in fruit orchards in whose inter-row spacings berries and greens are grown. The harvest time for cotton is 15 days, for hemp 20 days, and for all remaining crops 30 days. Olive trees may be treated only before they blossom, and mulberry trees before silkworms begin to feed. The tolerance level of dimethoate in fruits, including citrus ones, is 1 mg/kg.

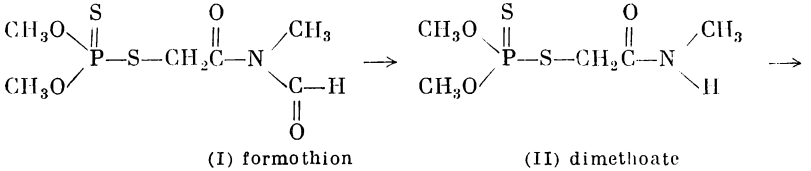
Formothion (Anthio)

The active ingredient is O,O-dimethyl-S-(N-methyl-N-formylcarbamoylmethyl) phosphorodithioate:

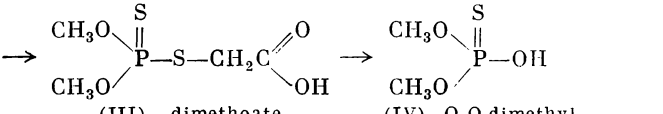


In the pure form, it is a crystalline substance melting at 25-26 °C, poorly soluble in water (2.6 g/litre at 24 °C) and well soluble in organic solvents.

In its chemical properties, formothion is similar to dimethoate, but is more stable when stored or heated. Ultraviolet radiation decomposes it into dimethoate. Hydrolysis in an aqueous medium proceeds as follows:



(I) formothion (II) dimethoate



(III) dimethoate carboxylic acid (IV) O,O-dimethyl phosphorothioic acid

Formothion rapidly decomposes both on the surface and inside plants, no residues of it are detected already on the eighth day, but

dimethoate is found in small amounts within up to 20 days. The decomposition of formothion in plants follows the path of hydrolysis in an aqueous medium. All its metabolites except dimethoate have no physiological activity, and their toxicity to animals is low. Formothion in its recommended doses causes no harm to plants.

This insecticide and acaricide has a high initial contact toxicity and a comparatively short systemic action. It is highly toxic to mites, sucking and mining insects, the younger larvae of various flies, sawflies, and *Lepidoptera*. After the use of formothion, bees and other beneficial insects also perish, but owing to the low persistence of the insecticide on the surface of plants, this action lasts only a short time.

The high systemic toxicity of formothion is explained by its metabolism in plants to dimethoate, whose toxicity is higher. In addition, metabolite IV is a synergist with respect to dimethoate. Consequently, pests are killed with a lower content of the insecticide in a plant.

Formothion is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 350 mg/kg) and is characterized by an acute dermal and weak cumulative effect.

Formothion is marketed in the form of a 25% emulsifiable concentrate. It is used in a concentration of 0.3-0.4% on cotton to control red spider mites, thrips, and aphids at a rate of use of the formulation of 2-2.5 kg (0.5-0.6 kg a.i.) per hectare; on sugar beets to control aphids, bugs, leafhoppers, and leaf miners at a rate of 1.2-1.6 kg (0.3-0.4 kg a.i.) per hectare; on fruit, including citrus, crops, hops, and cabbage to control a group of pests as a substitute for dimethoate, in a concentration of 0.1-0.2%; on grapevines to control mites and the larvae of mealybugs—of 0.2%, and on tea plantations to control tea moths, aphids, and cushion scale—of 0.1-0.2%.

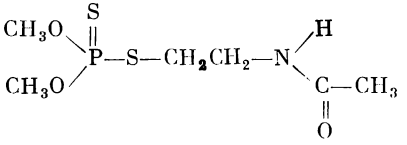
The rate of use of the insecticide on apples, pears, plums, cherries and grapevines is 1.2-4 kg (0.3-1 kg a.i.) per hectare; on citrus fruits it is 2.2-6 kg (0.5-1.5 kg a.i.) per hectare; on cabbage it is 0.8-1 kg (0.2-0.25 kg a.i.) per hectare; on hops it is 1.5-6 kg (0.4-1.5 kg a.i.) per hectare; on adult tea plantations it is 5-6 kg (1.3-1.5 kg a.i.) per hectare; and on young tea plantations it is 2-4 kg (0.5-1 kg a.i.) per hectare.

Formothion in its effectiveness is not inferior to dimethoate and has a number of advantages over the latter: a less acute toxicity to humans and animals, a low persistence of the substance in plants, and a weaker odour.

The harvest time for all agricultural crops is 20 days. On tea plantations, spraying should be performed after the last gathering of the tea leaves. The tolerance level of formothion in all food products is 0.2 mg/kg.

DAEP (Amiphos)

The active ingredient is O,O-dimethyl-S-2-(acetylamido) ethyl phosphorodithioate:



It is a colourless crystalline substance melting at 22-23 °C, poorly soluble in water and well soluble in organic solvents.

Its thermal stability is slight, and it rapidly decomposes in the light at an elevated temperature. In water, especially in an alkaline medium, it hydrolyzes to only slightly toxic products along the bond P—X.

The toxic residues of DAEP rapidly vanish from the surface of plants as a result of penetration of the substance into the tissues and its decomposition into compounds having a low toxicity. Upon penetrating into a plant through its leaves and roots, DAEP moves very well along the conveying system and exhibits systemic action. It is mainly decomposed in plants hydrolytically with the participation of phosphatases. Residues of the insecticide, however, were detected in 20-25 days after treatment. When properly used, the substance does not burn plants.

DAEP is an insecticide and acaricide with a high initial toxicity and with contact and systemic action. Its persistence ranges from 14 to 25 days. It is close to dimethoate in its spectrum of action, differing in its lower toxicity to mandibulate insects.

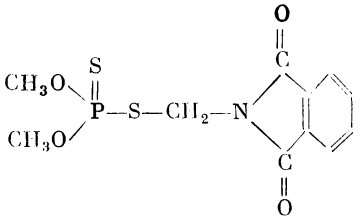
DAEP is moderately toxic to humans and animals (LD_{50} for rats is 475 mg/kg) and has a slight cumulative action. Its toxicity is lower than that of dimethoate.

It is recommended to use a 40% emulsifiable concentrate of DAEP on citrus crops to control mites, whiteflies, and the larvae of scales in a concentration of 0.2% at a rate of 4-6 kg (1.6-2.4 kg a.i.) per hectare; on sugar beets to control aphids, fleas, and leaf miners at a rate of 0.5-2 kg (0.2-0.8 kg a.i.) per hectare. When tested for controlling these pests, DAEP was not inferior in its effectiveness to dimethoate and formothion. The almost complete absence of an offensive sharp odour and the lower toxicity to humans allow DAEP to be used in populated areas. It is also used against sucking pests of cotton and grapes at a rate per hectare of 2.5 kg (1 kg a.i.) and 1.2-4 kg (0.5-1.6 kg a.i.), respectively.

The harvest time for citrus crops and sugar beets is 20 days, and for grapevines and cotton, 25 days.

Phosmet (Phthalophos, Imidan)

The active ingredient is O,O-dimethyl-S-{N-(mercaptomethyl) phthalimide} phosphorodithioate:



In the pure form, it is a white crystalline substance melting at 72-72.7 °C with an offensive odour, poorly soluble in water (25 mg/litre at 25 °C) and in aliphatic hydrocarbons. It dissolves well in most organic solvents.

Like other organophosphorus compounds, it readily hydrolyzes in an alkaline medium along the bond P—X to form dimethyl phosphorothioic acid, phthalimide, and formaldehyde. It is stable in an acid medium. Oxidizing agents decompose it with the formation of the oxygen analogue (the P=O analogue) as an intermediate, which is not inferior in toxicity to phosmet.

The substance persists in water basins up to 30 days and imparts an offensive taste and odour to the water.

Phosmet decomposes comparatively rapidly into products having a low toxicity in the soil, in plants, and on the surface of leaves. The metabolites excreted from plants include oxymethylphthalimide, phthalimide, phthaliminic, phthalic, oxybenzoic and benzoic acids, and benzamide. Its residues, however, are detected on plants in 21-32 days after spraying.

Phosmet penetrates poorly into a plant, especially through its leaves, which explains why it has no penetrating or systemic action. In the recommended concentrations, it has no phyticidal effect on a plant. According to data of research institutions, phosmet positively affects the general state of apple trees and does not change the aromatic and gustatory properties of the fruit.

Phosmet is a stomach and contact insecticide and acaricide with a relatively short protective effect (its persistence is 10-15 days). It is highly toxic to larvae and adult individuals of beetles, flies, and *Lepidoptera*. Its toxicity to these pests approaches that of carbaryl, is superior to the latter in its action on mites and sucking insects, but is inferior in its persistence.

Phosmet is highly toxic to humans and warm-blooded animals (LD_{50} for rats is 132.5 mg/kg) and has a slight chronic and dermal effect.

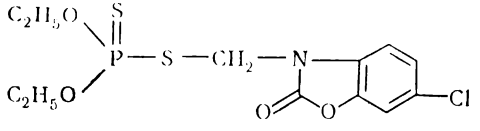
It is recommended to use a 20% emulsifiable concentrate and a 50% wettable powder of phosmet. Tests showed that these formulations have virtually the same effectiveness, but wettable powders are more convenient to work with. Phosmet formulations are used on sugar beets against common and gray beet weevils, mangold flea beetles, aphids, and larvae of leaf miners at a rate of use of the active ingredient of 0.5-1.5 kg/ha, and on potatoes against adult individuals of the first generation and larvae of the Colorado beetle at a rate of 0.8 kg/ha.

The effectiveness of phosmet on sugar beets was found to be superior to that of polychloropinene and toxaphene and ensured the extermination of 95-100% of the pests (the reference pesticides killed 50-70% of the pests). Killing of the gray beet weevil was observed simultaneously.

The treatment of field crops with phosmet formulations must be discontinued not later than 20 days before harvesting. The tolerance level of phosmet in water is 0.2 mg/litre.

Phosalone (Benzphos, Zolone)

The active ingredient is O,O-diethyl-S{-(6-chloro-2-oxo-benzoxazolin-3-yl)-methyl} phosphorodithioate:



In the pure form, it is a white crystalline solid with a slight garlic odour melting at 45-48 °C. It is not volatile, dissolves poorly in water (about 10 mg/litre at room temperature) and well in many organic solvents.

Phosalone is relatively stable in acid and neutral media. In an alkaline solution, it rapidly hydrolyzes along the bond P—X to form diethyl phosphorothioic acid, 6-chlorobenzoxazolone, and formaldehyde. Oxidizing agents cause phosalone to transform into the more toxic P=O analogue that is relatively unstable and rapidly decomposes.

In the soil, on leaves, and inside plants, phosalone comparatively rapidly decomposes into its P=O analogue with the following hydrolysis to the corresponding phosphoric acids and 6-chlorobenzoxazolone. It has also been shown that the phosalone molecule in a plant may be decomposed along the N-methylene bond with the formation of N-glycoside-6-chlorobenzoxazolone. Its residues were detected in the soil in 18-21 days when 6 kg of the formulation were incorporated per hectare. Phosalone may persist in plants up to 30 days.

Phosalone penetrates through the cuticular layers of plants and accumulates in the skin of fruits and the cuticle of leaves. It is not virtually translocated along a plant. After spraying plants with phosalone, no burning of the leaves of trees, shrubs, and herbaceous plants is noted.

Phosalone is a stomach and contact insecticide and acaricide with a high initial toxicity and a prolonged protective action. It has a penetrating effect. Insects and their larvae are killed in the first 48 hours after treatment. It persists 15-21 days on an average, and sometimes up to 30 days. The pesticide is highly toxic to mandibulate insects (caterpillars of codling moths, leaf roller moths), mining and sucking pests, and also to some species of beetles and their larvae. Its toxicity is low to false caterpillars of sawflies and bees. A major advantage of this compound is the retaining of a high activity even at a low temperature of the air (of the order of 10-12 °C).

Phosalone is highly toxic to humans and warm-blooded animals (LD_{50} for rats with one oral administration is 108 mg/kg), and has only slight dermal and chronic toxicity. It rapidly decomposes in an animal's organism into non-toxic products and is not secreted with a nursing female's milk.

The marketed formulations are a 35% emulsifiable concentrate and a 30% wettable powder. When tested, these formulations did not differ in their effectiveness, persistence, and action on insects and plants. Consequently, they should be considered as equivalent. The formulations of phosalone are recommended in a 0.2% concentration for use on fruit crops against codling, leaf roller, fall web-worm, lackey, and gypsy moths, aphids, psyllids, spider and hawthorn mites, scales, and mealybugs; on citrus crops to control citrus red and rust mites, citrus whiteflies, San Jose, Japanese long, and citricola scales; on grapevines against vine and European grape moths, spider mites, and the larvae of scale insects and mealybugs; on hops to control spider mites and aphids. The rate of use of the active ingredient on apple and pear trees is 0.7-1.4, on plum and cherry trees 0.3-1, on hops 0.3, on grapevines 0.4-1, and on citrus trees 1.4-2.1 kg/ha. On cotton, the wettable powder formulation is used to control bollworms and spider mites at a rate of use of the active ingredient of 0.7-1 kg/ha; on potatoes and vegetable crops to control the Colorado beetle, aphids, and the larvae of *Lepidoptera* at a rate of 0.5-0.7 kg, on alfalfa seed plantations against sucking and mandibulate pests at a rate of 0.5-1 kg, and on tobacco to control aphids, moths, and thrips at a rate of 0.6-0.7 kg/ha; on winter wheat a 35% emulsifiable concentrate is used against rustic shoulder-knot moths, pentatomides, and aphids at a rate of 0.52-0.7 kg, and on sugar beets against beet weevils at a rate of 1.0-1.2 kg/ha.

The treatment of fruit orchards with phosalone substantially reduces the number of mining pests.

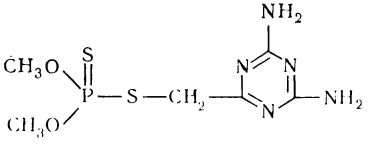
Phosalone has a larger spectrum of action and a larger persistence than phosmet. At the same time, it is inferior to phenthoate in its effectiveness against the larvae of scale insects and mealybugs. When used to control sucking and mining pests, the emulsifiable concentrate, which penetrates better into a plant, has a certain advantage.

The harvest time for fruit (including citrus) crops and grapes is 40 days, of hops is 20, of tobacco is 10, and of all other crops is 30 days.

The tolerance level of phosalone in food products of a vegetative origin is 0.2 mg/kg.

Menazon (Sayfos, Sayphos, Azidithion)

The active ingredient is O,O-dimethyl-S-(4,6-diamino-1,3,5-triazin-2-ylmethyl) phosphorodithioate:



In the pure state, it is a white crystalline solid with little or no odour melting at 160-162 °C, purely soluble in water (0.24 g/litre at 20 °C) and in most organic solvents. Menazon is thermally and chemically stable and is decomposed only slightly even by strong mineral acids and alkalies. Oxidizing agents transform it into the P=O analogue more toxic to organisms.

When it gets into the soil and water basins, menazon persists for a long time (in the soil up to a year, and in water up to two years) and may penetrate into the green organs of plants through their roots.

Menazon persists in the tissues of plants up to one month. Upon the storage of fruits containing residues of the insecticide, it decomposes at a still slower rate (three months). Decomposition is accelerated only upon heat treatment.

Menazon penetrates well into a plant through its roots and rapidly moves along the vascular system into the stem and leaves, accumulating in these organs in amounts that are toxic to insects. The insecticide penetrates to a smaller extent through the leaves, and almost no translocation farther than a treated leaf is observed. It has no negative effect on agricultural plants and on the organoleptic properties of food products.

Menazon is a highly selective systemic and contact insecticide with a prolonged protective effect. It is highly toxic to aphids, except

gall-forming ones, but does not virtually act on bees, silkworms, and other beneficial insects. It has only slight acaricidal properties. The duration of its protective action in treating seeds and other planting stock is 20-50 days, and after spraying green organs, it is 10-12 days and depends on the soil and climatic conditions. In the northern regions of the USSR, treatment of potato tubers with menazon protects the plants from damage by aphids during 40-50 days, and in the southern regions, during 15-20 days.

The substance has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 1260-1435 mg/kg), and has a slight chronic toxicity. The low toxicity of menazon and the absence of its accumulation in mammals' organisms are explained by the rapid decomposition and excretion of the substance from an organism. Already in two hours after it enters a rat's stomach, over 99% of the ingested insecticide decomposes.

The metabolism of menazon proceeds along an oxidizing and hydrolytic path through the formation initially of the less stable, but more toxic P=O analogue.

The industry produces an 80% powder and a 70% wettable powder of menazon. The former is used for treating seeds and planting stock by the semi-dry method: the seeds of leguminous crops at a rate of 10 kg (8 kg a.i.) per tonne; sugar beets at a rate of 2-4 kg (1.6-3.2 kg a.i.) per tonne; potato tubers at a rate of 2-2.5 kg (1.6-2 kg a.i.) per tonne. The wettable powder is sprayed during the vegetation period in a concentration of 0.05-0.1% in stone and pip fruit orchards at a rate of 1.0-2.8 kg (0.7-2 kg a.i.) per hectare; on vegetable, melon, and leguminous crops at a rate of 0.4-1.5 kg (0.3-1.0 kg a.i.), on potatoes—2.5-2.8 kg (1.7-2.0 kg a.i.), on sugar beets—0.6-1 kg (0.4-0.7 kg a.i.), on tobacco—0.8-2.0 kg (0.6-1.4 kg a.i.) per hectare.

Menazon is of special importance on crops subject to virus diseases whose pathogens are vectored by aphids. Menazon formulations have proved their high effectiveness in a system of measures for protecting potatoes against virus mosaic.

It is recommended to stop spraying orchards and vegetable crops with menazon formulations 20 days before harvesting.

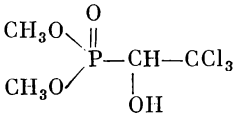
The tolerance level in food products of a vegetative origin is 1 mg/kg.

9. Phosphonic Acid Derivatives

The derivatives of phosphonic, phosphonothioic and phosphonodithioic acids include active insecticides and acaricides, fungicides and herbicides, but most of them are still in the stage of being studied, and only a few have found practical application. The most important of the phosphonic acid derivatives is trichlorfon.

Trichlorfon (Chlorofos, Dipterex, Dylox)

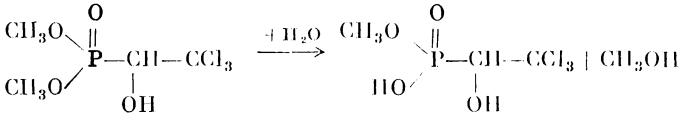
The active ingredient is O,O-dimethyl-(1-hydroxy-2,2,2-trichloroethyl) phosphonate:



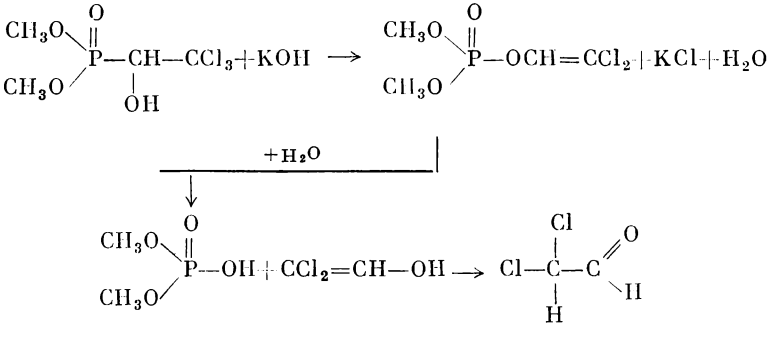
The pure substance is a white crystalline powder melting at 81-82 °C. It is well soluble in water (154 g/litre at 25 °C), benzene, chloroform, low-molecular alcohols, and chlorinated aromatic hydrocarbons; its volatility is 0.11 mg/m³.

The substance is very stable in the crystalline form at room temperature, but its aqueous solutions decompose. The rate of decomposition grows with an increasing pH of the solution. The insecticide decomposes especially rapidly in light in dilute solutions.

The hydrolysis of trichlorfon in various conditions follows two schemes. In an acid solution, the first hydrolysis product is O-methyl-(1-hydroxy-2,2,2-trichloroethyl) phosphonic acid, which further hydrolyzes with mineralization of the acid:



In an alkaline solution, trichlorfon becomes dehydrochlorinated and simultaneously regroups with the formation in the main of dichlorvos. The latter rapidly hydrolyzes into dimethyl phosphoric acid and dichloroacetaldehyde:



In natural conditions, trichlorfon rapidly decomposes into nontoxic metabolites. In the soil, this process is accelerated by the activ-

ity of microorganisms that demethylate the active ingredient into desmethyl-trichlorfon with the following formation of 2,2,2-trichloro-1-hydroxyethyl phosphonic acid. When trichlorfon is incorporated into the soil at a rate of 10 mg/kg, its residues are detected in the course of 15-112 days, depending on the kind of soil and the meteorological factors.

In water, the substance decomposes by dehydrochlorination and the formation of dichlorvos with its following hydrolysis. The process continues from a few days to two or three weeks.

Trichlorfon penetrates into plants through their roots and leaves, but owing to its rapid decomposition does not exhibit a prolonged effect.

Residues of the substance are detected on plants during from seven to ten days after treatment. The ability of the insecticide to migrate from the roots into the green organs of plants allows it to be used in the form of granules or by pouring under the roots for controlling cutworms and the maggots of cabbage and carrot flies.

Trichlorfon does not burn plants in its recommended concentrations, but in damp conditions it may damage the leaves and shoots, especially at a young age.

Trichlorfon is a stomach and contact insecticide with a high initial and a short protective effect (up to seven days). The stomach action is more pronounced than that of malathion, parathion-methyl, and diazinon. The substance can function partly as a fumigant. It has a quite broad spectrum of action: it is highly toxic to adult specimens and larvae of flies, *Lepidoptera*, *Hymenoptera*, and some beetles, and also to exo- and endoparasites of farm animals. It has a low toxicity to sucking pests (aphids, mites) and weevils. Since its contact effect is not high, trichlorfon is less harmful to beneficial entomofauna than other organophosphorus compounds.

Trichlorfon is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 630 mg/kg), it has slight cumulative properties, and may have a local irritative action on the skin. When it penetrates into an animal's organism, in addition to lowering of cholinesterase activity, changes are noted in the composition of the protein fraction of the blood, and the antitoxic function of the liver diminishes. The low toxicity of the substance to mammals is associated with the fact that trichlorfon rapidly decomposes in their organisms along the P—X and P—O(Alk) bonds to form products with a low toxicity excreted with the urine. This feature allows trichlorfon to be used in doses up to 30-40 mg/kg of live mass to control endoparasites of farm animals. But here great care must be taken to see that the farm products contain no residues of the pesticide.

When animals are treated, residues of the substance are found in their meat during two weeks, and in the milk of lactating animals, up to two days.

The metabolism of trichlorfon in organisms follows three main paths: dehydrochlorination, hydrolytic decomposition along the P—C bond, and hydrolysis along the P—O bond. The selectivity of the substance and its toxicity to organisms depend to a major extent on the direction of the process and the rate of the reactions.

The main direction of metabolism of trichlorfon in plants, insects, and animals is hydrolytic decomposition along the P—C bond occurring with the active participation of enzymes and with the formation of O,O-dimethylphosphoric acid and trichloroethanol (Fig. 11). This process takes place the most actively in the organism of a warm-blooded animal, especially in its liver, where the formed trichloroethanol conjugates with glucuronic acid and is excreted with the urine in the form of a glucuronide.

A characteristic process for warm-blooded animals is the hydrolytic demethylation with the formation of hydrolytically stable, but biologically inactive desmethyl-trichlorfon. This metabolite gradually decomposes under the action of microsomial enzymes to O-methyl phosphoric acid and trichloroethanol, which are readily excreted from the organism.

The comparatively low toxicity of trichlorfon to humans and animals is explained by the predominance of these two processes of its metabolism. The insecticide upon penetrating into an organism rapidly decomposes into non-toxic products.

In an insect's organism, the reaction of dehydrochlorination with the formation of the more toxic dichlorvos proceeds actively. The high insecticidal activity of trichlorfon can be explained in part by the predominance of this process. The stomach action of the insecticide is also probably associated with this reaction because it sharply accelerates in the alkaline medium of an insect's stomach.

Three formulations based on trichlorfon are marketed: an 80% technical product, an 80% wettable powder, and a 7% granulated formulation. The wettable powder does not become caked and in its effectiveness is not inferior to the technical product. Both formulations are used to spray grain crops against pentatomids and other bugs, and also against frit, gout, and Hessian flies, and cereal leaf beetles at a rate of 0.75-1.5 kg/ha; against corn weevils and rustic shoulder-knot moths at a rate of 2 kg (0.6-1.5 kg a.i.) per hectare; on rice against shore flies, rice midges, miners, and cereal leaf beetles at the same rate; on flax against large flax flea beetles; on cabbage against cabbage moth and diamond back moth maggots, cabbage butterflies, cruciferous-feeding bugs and flea beetles; on potatoes against the young larvae of Colorado beetles; on sunflowers against cutworms, on leguminous grass against moths, bean-seed flies, and bugs at a rate of 0.8-1.5 kg (0.6-1.2 kg a.i.) per hectare, on leguminous plants against pea beetles and codling moths; on sugar beets against fleas and cutworms at a rate of 1-1.5 kg (0.8-1.2 kg a.i.) per

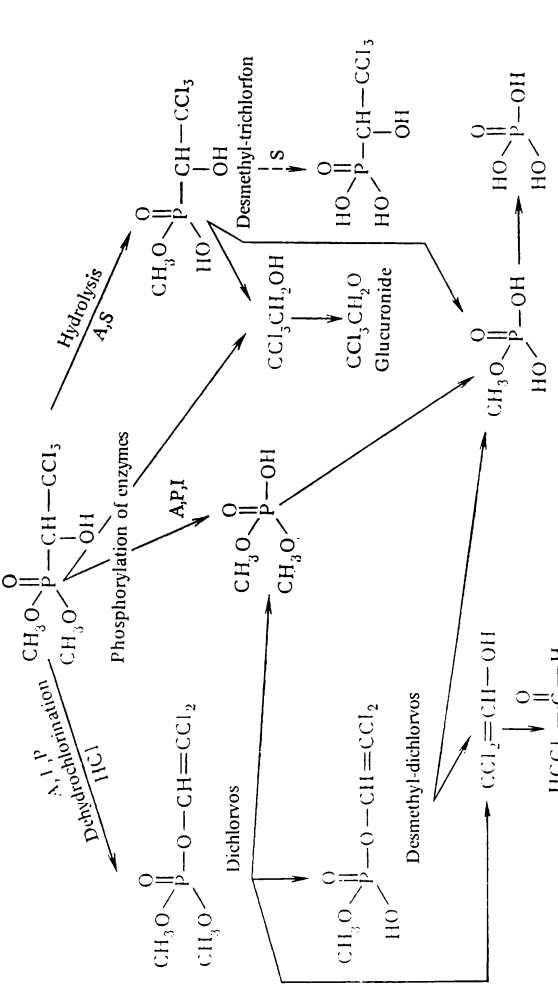


Fig. 11. Diagram of metabolism of trichlorfon (A = animal; I = insect; S = soil; P = plant)

hectare; on cotton against cutworms at a rate of 1.5-1.8 kg (1.2-1.4 kg a.i.) per hectare; on melons against cantaloupe and bean-seed flies at a rate of 1-2 kg (0.8-1.6 kg a.i.) per hectare; on castor-bean plants against moth caterpillars; on mustard against cruciferous-feeding flea beetles, bugs, white butterflies, leaf beetles, and saw-flies at a rate of 1.5-2 kg (1.2-1.6 kg a.i.) per hectare; on hemp at a rate of 1.2-2 kg (0.96-1.6 kg a.i.) per hectare; in orchards (apple, pear, plum, cherry) against pierid butterfly caterpillars, brown-tail, gypsy, lackey, codling, apple, leaf roller, and fall web-worm moths, false caterpillars of sawflies and larvae of cherry fruit flies; on grapevines against vine bud and leaf roller moths in a concentration of 0.2-0.3% of the formulation at a rate of use of the latter of 1.6-6 kg (1.3-4.8 kg a.i.) per hectare; in orchards against wood and apple clearwing moths after harvesting the crop in a concentration of 0.8% at a rate of use up to 16 kg (13 kg a.i.) per hectare. In empty granaries, trichlorfon is used for the moist disinfection against grain pests at a rate of 4 g (3.2 g a.i.) per m^2.

Granulated trichlorfon is the main means for controlling European cornborers by aerial spraying of the plantings in the phase of blossoming of the corn at a rate of 20-40 kg (1.4-2.8 kg a.i.) per hectare. In addition, this formulation is used for incorporation into the soil when sowing vegetable crops to control cabbage and onion maggots, carrot rust-flies, and blue fleas, when sowing melons to control bean-seed flies, and when sowing potatoes to control cutworms at a rate of use of 50 kg (3.5 kg a.i.) per hectare. To control overwintered pentatomid bugs, granulated trichlorfon is applied to the edges of forests and forest belts at a rate of 40-100 kg (2.8-7 kg a.i.) per hectare. Aerial spraying with trichlorfon using the solvent at a rate of 25-50 litre/ha is widely employed to eradicate the pests of field crops.

Notwithstanding the relatively low toxicity of trichlorfon to humans, its use in agriculture is strictly regulated. The treatment of orchards, grapevines, field, vegetable, melon, and technical crops must be terminated at least 20 days, of cereal, corn, and leguminous crops—15 days before harvesting, and castor-bean plants and mustard—before blossoming. Granaries must be treated at least 10 days before filling them. The tolerance level of trichlorfon in vegetable food products is 0.2 mg/kg. In food products of an animal origin, no residues are tolerated.

6.1.3. Carbamic Acid Derivatives

1. Aryl Esters of Alkyl Carbamic Acids

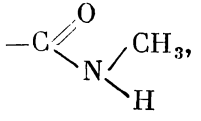
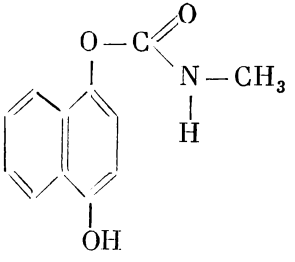
The substances of this group include highly active insecticides, fungicides, and herbicides. Only esters of N-alkyl carbamic acids, however, have insecticidal properties. The substitution of the second

hydrogen atom at the nitrogen by an alkyl radical sharply decreases the insecticidal activity of the compounds. The only exception are esters of N,N-dimethyl carbamic acid with complex heterocyclic hydroxy compounds.

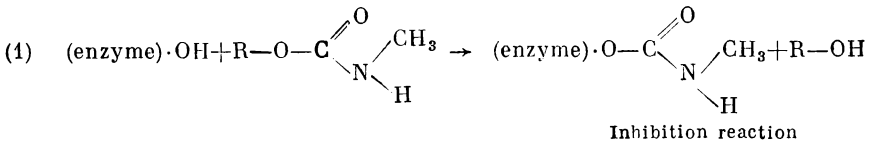
The highest activity is exhibited by aryl esters of N-methyl carbamic acid.

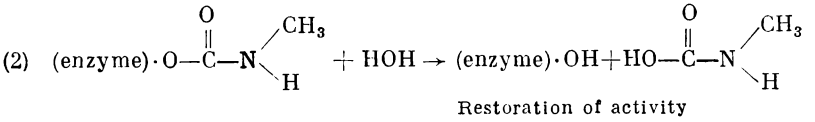
N-methylaryl carbamates are substances that are stable in sunlight and in storage, as well as in neutral and acid media. They readily hydrolyze in alkalies with the detachment of an aryl group and the following decomposition of the acid residue into CO_2 and simple amines. They persist from 14 to 40 days on the surface of treated plants.

Insecticides of this group can penetrate through the leaves and root system of plants, but have no systemic action. They have no adverse effect on the growth and development of agricultural crops and do not lower their yield. Like other carbamates, however, in high doses they inhibit the processes of root cell division, causing the perishing of the root hairs.

The main path of metabolism of N-methylaryl carbamates in a plant is hydrolysis with detachment of the group  , which then decomposes into CO_2 and NH_3. In addition, the hydrogen atoms in the ring are substituted by hydroxyl groups with the formation of metabolites of the type  and the following decomposition of the aromatic ring. The formed free phenols and other products of decomposition of N-methylaryl carbamates can be included in the general scheme of metabolism of the plants. The volatile products (CO_2) are evolved via the stomas.

The aryl esters of N-methyl carbamic acid are highly active contact and stomach insecticides with a broad spectrum of action. The mechanism of action of these substances on insects and animals consists in inhibiting the activity of the enzyme acetylcholinesterase in the nerve tissues:



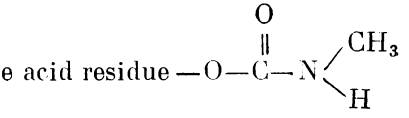


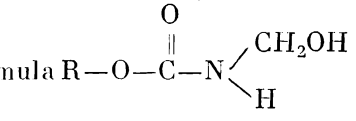
The inhibition of the activity of acetylcholinesterase in the nerve tissues is attended by the accumulation of acetylcholine, which violates the function of the nervous system. The result is paralysis and perishing of the insects.

The activity of the enzyme is restored slowly, although more rapidly than in poisoning by organophosphorus compounds. This is why the paralysis of insects is an irreversible phenomenon.

The anticholinesterase activity of N-methylaryl carbamates, unlike that of organophosphorus compounds, increases with a growth in the hydrolytic stability of the substance and depends on its chemical structure and the spatial arrangement of the individual groups in a molecule.

In an insect's organism, N-methylaryl carbamates rapidly metabolize in three main directions:

(1) hydrolysis with detachment of the acid residue  and the formation of free phenols;

(2) oxidation of the alkyl radical in the acid group with formation of compounds of the general formula  and the following demethylation;

(3) hydroxylation of the aromatic ring with the formation of conjugates with glutathione.

The products formed in the second and third reactions have anticholinesterase properties, but are less stable and rapidly decompose into non-toxic products. The toxicity of N-methylaryl carbamates can be increased if substances inhibiting the reactions of insecticide decomposition (piperonyl butoxide, sesamex) are introduced into an insect's organism.

Upon the perennial application of carbamate insecticides, insects acquire specific group resistance to these compounds.

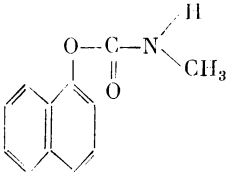
The resistant specimens are distinguished by a high rate of decomposition of the carbamates into non-toxic products.

There has also been noted the appearance of cross resistance to carbaryl, organochlorine compounds, carbamates, and organophosphorus compounds.

Most insecticides that are derivatives of N-methyl carbamic acid are highly toxic to humans and animals (LD_{50} for rats is 16-250 mg/kg). Exceptions are carbaryl and 3-isopropylphenyl-N-methyl carbamate. When ingested into human and animal organisms even in small doses, carbamates have a negative action on the neurohumoral and endocrine systems and exhibit embryotoxic and mutagenic action. With a view to these properties of N-methylaryl carbamates, their use is strictly limited in the USSR, and only carbaryl and pirimicarb may be used with the relevant restrictions.

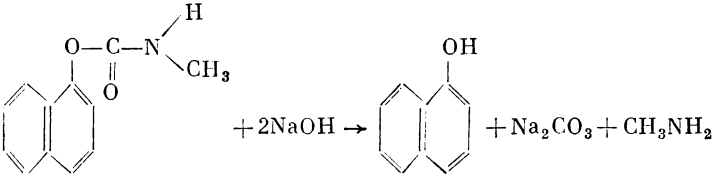
Carbaryl (Sevin)

The active ingredient is 1-naphthyl-N-methyl carbamate:



Chemically pure carbaryl is a white crystalline odourless solid melting at 142 °C. It dissolves poorly in water (less than 0.1% at 20 °C) and well in organic solvents.

It is stable to light, in an aqueous medium, at elevated temperatures (up to 70 °C), and in storage. In an alkaline medium (pH 10), carbaryl rapidly hydrolyzes to 1-naphthol:



This feature underlies the colorimetric method of determining carbaryl residues in various media.

The insecticide persists in the soil one or two years and can migrate from it to other objects of the environment: into plants, water, and the air. The prolonged presence of carbaryl in the soil in an amount of 1-2 mg/kg leads to the extermination of the *Protozoa* and algae and to an increase in the activity of ammonizing bacteria. With large doses, this stimulation gives way to depression, and the nitrifying

activity grows. The soil contains races of microorganisms capable of decomposing carbaryl.

When properly used, carbaryl does not damage cultivated plants, does not lower the yield, and does not detract from the taste and odour of products. Burning of young leaves is noted only at a high humidity and temperature of the air. When apple trees are sprayed immediately after blossoming, falling of the young fruit is observed. For this reason, orchards may be treated with carbaryl only in a month after blossoming. The insecticide is very persistent on the leaves of plants, on grapes and all kinds of fruits. Its residues are detected even in one to three months after application.

Carbaryl easily penetrates through the roots of plants and moves into their green organs up to the generative ones. It is decomposed in plants as shown in Fig. 12.

The main process in the metabolism of carbaryl in plants is hydrolysis. It occurs either without enzymes, or with the participation of various hydrogenases, first of all amylases. Oxidation processes with the following N-dealkylation and hydroxylation requiring the expenditure of energy and a hydrogen donor may occur simultaneously. One of the metabolites—5-hydroxynaphthyl-N-methyl carbamate—is more toxic than the initial substance, i.e. activation occurs. This metabolite, however, is less stable and rapidly decomposes into products with a low toxicity.

The products of hydrolysis and hydroxylation are mainly less toxic and less stable than carbaryl, and do not accumulate in plants. The detoxication processes, however, proceed very slowly in plants and are accelerated insignificantly in the processing of fruits and vegetables. Upon heat treatment, the residues of carbaryl in fruits lower by 45-90%, and in the preparation of juices, by 50-53%.

In sourcrout during five months of storage, its content decreased only by 25%.

Carbaryl is a stomach and contact insecticide. It is a good killer of adults and larvae of beetles, *Lepidoptera*, *Diptera*, thrips, and bugs. It has a positive temperature coefficient. When it penetrates through the roots, it has a systemic action.

Like other N-methylaryl carbamates, carbaryl kills insects by violating the functions of their nervous system as a result of inhibition of acetylcholinesterase. This is why it has no selectivity and exterminates beneficial insects, including bees, carabids, and earthworms. At the same time, carbaryl is virtually non-toxic to phytophagous mites, therefore after treatment with carbaryl, outbreaks of mite reproduction are frequently observed in plantings of agricultural crops because of the extermination of predatory insects and the changes in the conditions of feeding.

Carbaryl is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 560 mg/kg). When it enters an organism, it rapidly

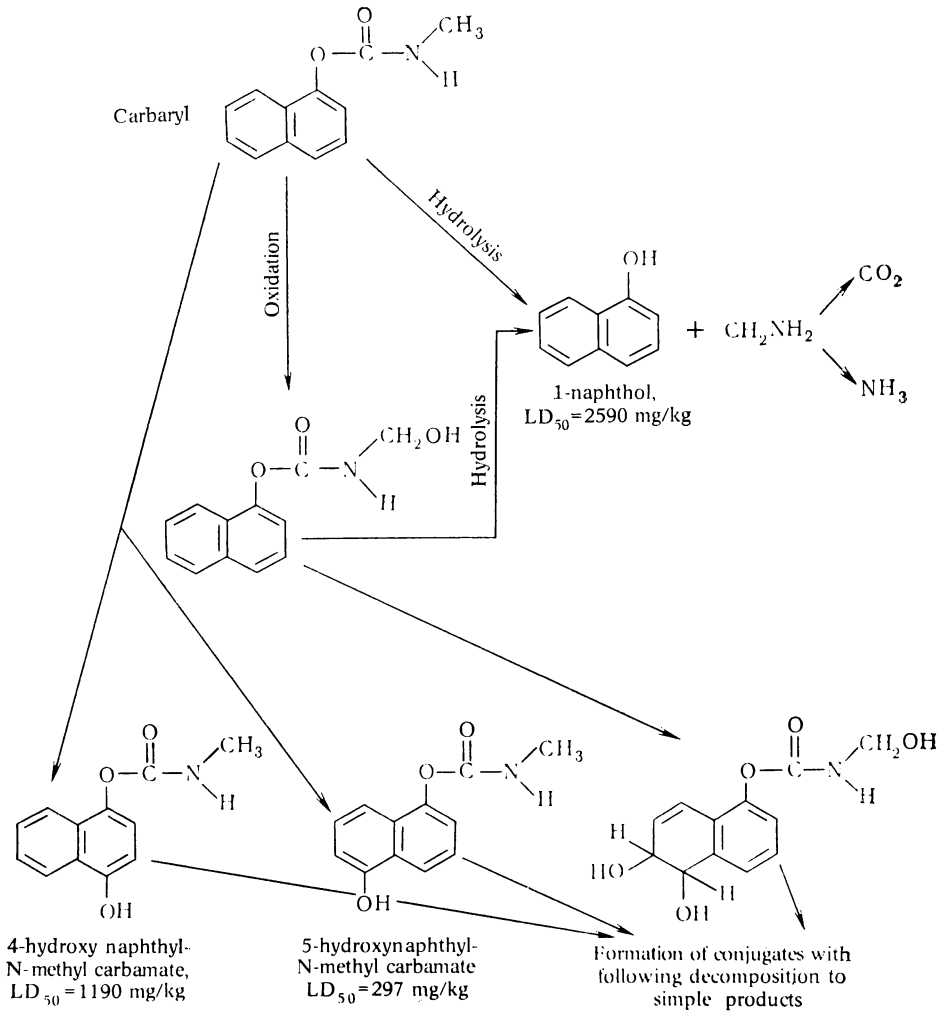


Fig. 12. Diagram of metabolism of carbaryl

penetrates into the blood and is carried to all parts of the body, causing a sharp suppression of the cholinesterases.

The indications of poisoning by carbaryl are typical of poisoning by anticholinesterase substances. The nervous system is the first to be affected.

The chronic toxicity of the insecticide is slight because it rapidly decomposes (mainly in the liver) into water-soluble non-toxic prod-

ucts. In 48 hours, only traces of carbaryl are detected in the tissues. The decomposition products are actively excreted with the urine and feces.

The main ways of detoxication of carbaryl are hydrolysis to 1-naphthol, which is rapidly excreted with the urine, and hydroxylation of the naphthol ring with its following decomposition. In an animal's organism, oxidation of the methyl group of the oxygen residue and the formation of conjugates with glucuronic and sulphuric acids excreted with the urine may also occur.

Owing to its rapid decomposition and the excretion of the products of its metabolism from organisms, no carbaryl residues are detected in livestock products.

The dermal and inhalation toxicity of the insecticide is insignificant.

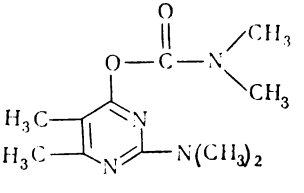
Investigation of the remote effects of the action of carbaryl on the organisms of warm-blooded animals has shown that in a chronic test the insecticide has a gonadotropic, embryotoxic, and mutagenic action already at a dose of 0.5 mg/kg. Here the neurohumoral and endocrine systems of an organism are harmed. In doses of 3-50 mg/kg, it exhibits a teratogenic action. In this connection, the use of carbaryl in the USSR is appreciably restricted, and no residues of it in food products are tolerated.

The industry produces an 85% wettable powder of carbaryl (naphthyl carbamate). 0.2-0.25% suspensions of carbaryl are used to control apple worms at the sites of their mass reproduction, on corn to control frit flies and European cornborers, and on cotton to control bollworms, armyworms, and hollyhock seed moths.

The rate of use of the insecticide is 1-2.5 kg (0.8-2.1 kg a.i.) per hectare. The harvest time is 45 days for orchards, and 20 days for cotton and corn. No residues of carbaryl in fruits and berries, corn, and cotton seeds are tolerated.

Pirimicarb (Pirimor, Aphox)

The active ingredient is N,N-dimethyl-(5,6-dimethyl-2-dimethylamino-4-pyrimidinyl) carbamate:



The chemically pure compound is a colourless odourless solid melting at 90.5 °C. It dissolves poorly in water (2.7 g/litre at 25 °C)

and well in organic solvents. It rapidly decomposes in an aqueous medium and on treated surfaces.

The insecticide is not phytotoxic, and does not damage flowers, fruits, or leaves.

Pirimicarb is a contact, fumigational, and systemic insecticide highly active against all species of aphids and is distinguished by its rapidity of action. A systemic effect manifests itself when it penetrates through the roots. When plants are sprayed, the insecticide moves only within the confines of one leaf. It has a low toxicity to bees and entomophags of aphids (lacewings and ladybirds), which allows it to be used on blossoming crops and in integrated pest management systems.

It is highly toxic to humans and warm-blooded animals (LD_{50} for rats is 111 mg/kg), while its dermal, irritating, and cumulative properties are only slight.

The pilot use of a 50% wettable powder of pirimicarb is permitted for controlling aphids especially resistant to organophosphorus compounds, on cotton and on potato seed plantations at a rate of 1.5-2 kg of the formulation (0.7-1 kg a.i.) per hectare; on sugar beet transplantations at a rate of 0.6 kg, on peas (except green peas) at a rate of 1.5 kg of the formulation (0.75 kg a.i.) per hectare. It is permitted to spray potatoes and sugar beet transplantations during the vegetation period, cotton up to opening of the bolls, and peas not later than 30 days prior to harvesting. It is prohibited to use potatoes from treated fields for food purposes.

The concentration of the insecticide in the air of a working zone must never exceed 0.2 mg/m^3.

6.1.4. Nitrophenols

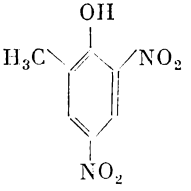
Most nitrophenols have a high biological activity. They are highly toxic to insects, bacteria, and fungi in all stages of their development, to green plants, and warm-blooded animals. This universal nature of the action of nitrophenols is explained by their ability, when penetrating into an organism, to separate the processes of respiratory phosphorylation, causing hydrolysis of the intermediates, and to stimulate the hydrolysis of adenosine triphosphoric acid in the course of reactions of the respiratory chain. Since these processes are common to all organisms, the toxicity of nitrophenols fluctuates only depending on the rate of its penetration into and excretion from an organism.

The process of deactivation of nitrophenols takes place in various organisms through the reduction of the nitrogroups to aminogroups with the following detachment of the latter and decomposition of the ring. In addition, nitrogroups may also be detached.

Nitrophenols belong to substances that are highly poisonous to humans and warm-blooded animals, and have a chronic toxicity and an acute dermal action.

DNOC (Sinox)

The active ingredient is 2-methyl-4,6-dinitrophenol:



It is a yellowish odourless crystalline solid melting at 86.4 °C. It dissolves poorly in water (130 mg/litre at 10 °C) and well in most organic solvents.

With caustic alkalies, ammonia, and organic amines, DNOC forms salts soluble in water, which in the dry form easily explode as a result of percussion or detonation. When reacted with reducing agents, the nitrogroup is reduced to $-NH_2$.

DNOC is quite persistent on treated surfaces and vanishes from them under the action of meteorological factors. It decomposes comparatively rapidly in the soil either as a result of sequential reduction or because of detachment of a nitrogroup with the following decomposition of the ring.

DNOC burns green plants, especially dicotyledonous ones. Opening leaf buds, young green shoots, ovaries, and flower buds are very sensitive to it. When young dormant trees are treated, growth inhibition and burns of the young bark are sometimes observed.

The toxicity to plants increases with elevation of the temperature of the air.

DNOC is a contact insecticide. It destroys wintering stages of pests (scale, eggs of aphids, psyllids, and mites). It also has a fungicidal and herbicidal action.

It is highly toxic to humans and warm-blooded animals (LD_{50} for rats is 40-85 mg/kg). It has pronounced cumulative properties and acute dermal toxicity. DNOC may penetrate into an organism through the respiratory and gastro-intestinal tracts, the undamaged skin, and the mucous membranes. It is excreted from an organism slowly (during a day from 1 to 20% of a single ingested dose), which is why it may cause chronic poisoning because of material cumulation. The compound strongly dyes the skin and clothes yellow. Poisoning by DNOC is characterized by a bronze colour of the hair and skin on the arms, and the appearance of a yellow colour in the urine. The cardiac activity and the blood pressure sharply drop.

The marketed product is a 40% water-soluble powder of DNOC-ammonium. To reduce the explosion hazard, inorganic diluents (sodium or ammonium sulphate, urea, etc.) are added to the compound.

The insecticide is used to exterminate the eggs of aphids, psyllids, and mites, and also scales on fruit trees, grapevines, gooseberries and currants by ample spraying (washing) with a 1% solution in the dormant period (early spring). The rate of use of the compound is 8-20 kg (3.2-8 kg a.i.) per hectare. The treatment periods must be observed very strictly, otherwise individual twigs, buds, or even whole trees may perish. Spraying is permitted at a temperature of the air not over 20 °C. No residues of DNOC in food products are tolerated.

Nitrafen

This compound is the product of nitration of shale phenols. The nitration process is continued until a substance is obtained that contains 1.5 nitrogroups per phenol molecule. The technical product is a dark brown pasty substance with a pungent odour of carbolic acid. It dissolves well in water.

In its chemical properties and biological activity, it is identical to DNOC, but has a stronger fungitoxic property (it eradicates the wintering phases of pathogens from the group of downy mildew) and a lower toxicity to humans.

It is marketed in the form of a 60% paste, and is applied in the early spring before opening of the buds in orchards, on grapevines, and in berry plantations by spraying with a 2-3% solution. The rate of use of the substance is 30-60 kg/ha. It is a good destroyer of the eggs of aphids and mites, scale, and also of pathogens (apple and pear scab, grape mildew, anthracnose and septoria spot of currants, gooseberry powdery mildew).

Nitrafen is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 800 mg/kg). It persists in animals' organisms, however, considerably longer than the other nitrophenols. Upon a single ingestion (400 mg/kg) into a rat's stomach, nitrafen already in two hours is found in the blood and circulates in it during 14-16 days.

No residual amounts of nitrafen are tolerated in food products.

6.1.5. Mineral Oils

Mineral oils are produced in the refining of petroleum, and in the processing of pit coal, lignites, oil shale, and peat. The use of pesticides based on coal oils is prohibited in the USSR because they have pronounced dermal and cancerogenic action.

Petroleum Oils

Petroleum mineral oils are a mixture of various hydrocarbons, therefore the toxic properties of the oils depend on the composition and structure of these hydrocarbons. They are obtained in the process of fuel oil distillation at a temperature from 275 to 450 °C, and green oil, in the pyrolysis of petroleum products.

With respect to their boiling point, viscosity, and density, petroleum oils are classified into light (boiling point 275-300 °C), medium, and heavy (boiling point 300-450 °C). Light oils include vaseline, transformer, and solar (diesel fuel) oils having a density over 0.84 g/ml and a viscosity of 1.3-1.75 Engler degrees at 50 °C; medium oils include spindle oils with a density of 0.895-0.905 g/ml and a viscosity of 2.8-3.2 deg, and heavy oils include machine and cylinder oils with a density over 0.9 g/ml and a viscosity of 1.8-8.5 Engler degrees at 50 °C.

Light oils mainly contain saturated hydrocarbons of the fatty series, and medium oils—naphthenes. In heavy oils, the content of aromatic compounds grows sharply. The differences in the composition of mineral oils underlie their different chemical and toxic properties.

Paraffin and naphthene hydrocarbons are chemically more stable, oxidize slowly in the air, are distributed better over the surface of plants' coatings and insects' integuments, penetrate well through the wax scales of insects, but are less toxic. Aromatic and unsaturated hydrocarbons rapidly oxidize under the action of the oxygen and ozone in the atmospheric air to form acids causing strong burns of plants. The process is sharply intensified under the influence of solar radiation. These compounds are easily sulphonated in the presence of H_2SO_4, are distributed more poorly over surfaces, but are more toxic to insects and plants. Plants are protected with distillates of various petroleums consisting of methane-naphthene and aromatic hydrocarbons. Here a combination of the positive properties of these compounds is achieved: the methane and naphthene hydrocarbons improve the penetration of the more toxic oils under the scales of insects and lower the phytotoxicity of the insecticide.

The phytotoxicity of petroleum oils depends on their content of aromatic (C_a) and naphthene (C_n) hydrocarbons. It has been established that mineral oils containing less than 10% of aromatic hydrocarbons do not have a noticeable negative effect on a plant. At a value of C_a/C_n below 0.2, petroleum products have a low phytotoxicity.

We have already noted that plants are burned under the action of acids formed in the light with the participation of oxygen. Plants may also be damaged, however, when oils are used with a low content of aromatic hydrocarbons, but containing solid paraffins (solidifying at 14-15 °C). Penetrating together with the oil into plants' tissues,

the paraffins solidify even at summer temperatures, which leads to rupture of the tissues and choking of the vessels. For this reason, the content of solid paraffins in petroleum products used for summer treatments must never exceed 5%.

Owing to their high phytocidal action, petroleum mineral oils are not used for treating herbaceous plants. Fruit trees, especially when dormant, endure spraying with oils quite well. The most sensitive are stone, citrus, and berry plants, and the least sensitive, pip fruit trees. Late autumn spraying lowers the resistance of the trees to cold, therefore it is performed in regions with a mild winter not earlier than in two months after defoliation at a temperature above 5 °C.

Petroleum oils are contact insecticides and acaricides with a short protective period. They are highly toxic to scales, mealybugs, and mites. The ovicidal properties are not adequate (except for green oil), therefore the toxic properties of oils are improved by adding organophosphorus insecticides and acaricides, for example, trichlorometafos-3. Some kinds of oils are effective as fungicides.

The toxic action of petroleum oils on insects, mites, and their eggs is mainly due to violation of gas exchange and the water balance of an organism. This is confirmed by the high activity of oils with a large content of paraffins and isoparaffins that are stable to oxidation and can produce stable films on a treated surface. The toxicants, spreading very well over a surface, form stable shells preventing metabolism in an egg or in an insect's body. In addition, oils destroy the integuments of insects and egg shells, readily penetrate through wax scale and cuticles, violating the structure of the internal tissues and the course of enzyme processes, and also causing coagulation of the cytoplasma. To ensure a high effectiveness of petroleum oils, thorough covering of plants' surfaces is essential, especially when controlling wintering stages of pests.

Petroleum oils have a low toxicity to humans and warm-blooded animals, but may cause irritation of the mucous membranes. They have pronounced locally irritating properties. When they get onto the skin, they cause dermatitis, eczemas, and folliculitis. They are toxic when they enter the respiratory tracts in the form of aerosols or vapour.

Several formulations based on petroleum oils are available. The greatest favour has been found by formulations of petroleum-oil emulsions No. 30, 30s, 30a, 30m, and 30ss, distinguished by a different content of aromatic and unsaturated hydrocarbons (the sulphonating fraction of the oil). Formulation No. 30 contains 40% of a paraffinous distillate of high-grade Surukhan petroleum, 40% of transformer oil, 2% of sulphite liquor, 0.5% of OP-7, and 17.5% of water. The C_a/C_n ratio for paraffinous distillate and transformer oil is 0.25, therefore the formulation may cause the burning of plants.

In formulation No. 30s, the transformer oil has been replaced with sulphonated solar distillate from heavy Balakhan petroleum having a lower phytotoxicity ($C_a/C_n = 0.125$). Formulation No. 30a, which contains 80% of a non-sulphonating residue, 17.5% of water, 2% of sulphite liquor, and 0.5% of OP-7, has a still lower burning action. Formulation No. 30m also has a lower phytocidal activity.

Formulation No. 30 is recommended for controlling scales, aphids, psyllids, and mealybugs by spraying in the early spring at a concentration of 3-4%, and in summer, 2-3%. The rates of use of the formulation are 40-100 litre/ha in early spring spraying of apple and pear trees before opening of their buds at an air temperature of not lower than 4 °C, and of citrus trees over dormant buds. This treatment simultaneously destroys the eggs and larvae of fruit tree spider, gooseberry, and citrus red mites. It must be noted that the ovicidal action of these substances is inadequate, but they are indispensable against the San Jose scale. The harvest time is seven days.

Petroleum oil emulsions can be prepared directly at farms. For this purpose, emulsifiers (clay, naphtha soap, green or blue vitriol and the like) are added to the oil. Depending on their physical properties and chemical composition, petroleum oils are divided into **summer** (for spraying in spring) and **winter** (for early spring and late autumn treatments) oils. Summer oils are less phytocidal, less viscous, and contain 95% of non-sulphonating substances. Winter oils contain 85% of these substances, they are more viscous and phytocidal.

The summer oils include vaseline and transformer oils, and diesel fuel, the winter ones include machine, solar, spindle, and green oils.

To prepare petroleum oil emulsions, one must take: (1) 10 kg of naphtha soap and 20 litres of warm water per 70 kg of winter oil; (2) 25 kg of fine rich clay and 25 litres of water per 50 kg of winter or summer oil; or (3) 2.5 kg of green or blue vitriol, 1 kg of freshly slaked lime, and 50 litres of water per 100 kg of oil. The mixtures are thoroughly stirred to obtain a homogeneous compound and are diluted with water to the required concentration.

Winter oils are used in the form of petroleum oil emulsions in a concentration of 4-6% for stone fruit trees, of 6-8% for pip fruit trees, and summer oils in a 1% concentration for deciduous fruit trees and in a 2% concentration for citrus trees. Upon early spring treatment, thorough washing of the trees is required. The rate of use in apple and pear orchards and on citrus trees is 20-100 litre/ha. The compounds are effective against wintering stages of pests: scale, mealybugs, the eggs of psyllids, aphids, and mites, and leaf roller moth caterpillars.

The phytotoxicity of the oils is higher, however, than that of formulation No. 30, therefore their perennial use may cause inhibition of trees and shrubs. Oils may be used for treatment only up to opening of the buds.

6.2. Rodenticides

Both inorganic (zinc phosphide) and organic compounds are used as rodenticides. They all kill rodents when they penetrate through the gastro-intestinal tract, although the mechanism of action of each pesticide is different.

Rodenticides are mainly used for preparing poisoned baits.

Grains of oats, wheat, rye, corn, etc. are used as the bait material for controlling gophers, voles, midday gerbils and mice in field conditions. Grain bait can be used to control voles only in cold weather. In summer, they do not eat such bait. To eradicate them in warm weather, and also the great gerbil in spring and autumn, green bait is used such as alfalfa, clover, and other succulent food.

To exterminate rats and mice in premises (granaries, livestock buildings, greenhouses, etc.), bread crumbs, porridge, grain, minced meat and fish, etc. are used as the bait. At stock-raising farms, bait is prepared on the fodder forming the ration of the livestock and is placed in the feed bunks in stalls freed of animals.

Baits must include adhesives (stickers). Vegetable oils are the best for this purpose. In controlling gophers, motor oil (No. 10 and No. 5) is mainly used as the adhesive.

Water-soluble poisons are used in the form of aqueous solutions, and the bait is soaked in them.

A very small assortment of substances is used in practice for poisoned baits. This is associated with the difficulty of preparing substances with a narrow selective toxicity.

Zinc Phosphide (Phosvin)

The active ingredient is Zn_3P_2. The pure substance is a dark gray odourless powder with a high melting point. It is insoluble in water and ethanol, and soluble in benzene and carbon disulphide. It is thermally stable.

When reacted with acids, even weak organic ones, zinc phosphide decomposes with the evolution of the very poisonous phosphine, capable of spontaneous flammation:

$$Zn_3P_2 + 6HCl \rightarrow 2PH_3 + 3ZnCl_2$$

Such a process also occurs in an animal's stomach upon the souring of baits consisting of bread, dough, porridge, or greens. Such baits lose their toxic properties in a few days.

Zinc phosphide decomposes comparatively slowly in other poisoned baits, and their toxicity persists during a month and more. Consequently, when zinc phosphide is used, domestic and wild animals and birds may be poisoned.

The toxic action of zinc phosphide on rodents is due to the fact that when it is ingested into the stomach, it decomposes into phosphine, which is the toxic substance. Phosphine penetrates with the blood stream into the animal's nervous system and results in violation of its functions. The death of animals is preceded by vomiting, weakening of the heart's activity, emphysema, and convulsions.

The toxicity of zinc phosphide to rodents depends on the quality of the poison and on the natural resistance of the animals to its action. The quality of the rodenticide is determined by the fineness of grinding, which underlies the dimensions of the poison's reactive surface coming into contact with the acid in an animal's stomach. Finer particles accelerate and amplify the action of the poison. The fineness of grinding is determined by the relevant USSR State Standard.

The resistance of rodents to zinc phosphide depends on their mass, physiological state, age, and specific features. Animals with a high vitality (in the period of intensive reproduction) are more resistant to poisons.

The specific resistance of rodents to zinc phosphide is associated with the features of their feeding. The high resistance of gophers is apparently explained by the lower acidity of their gastric juice. The amount of acid evolved in the stomach depends on the composition and quality of the food and on the time when it enters the stomach. It has been established that the more the food corresponds to the needs of rodents in the given conditions of their existence, the higher is the acidity of their gastric juice and the more rapidly does poisoning with zinc phosphide occur.

Baits with zinc phosphide have no repelling taste or odour and are readily eaten by rodents.

As regards its toxicity to humans and warm-blooded animals, zinc phosphide belongs to strong poisons with selective toxicity; it has no chronic toxicity. It completely decomposes in the stomachs of killed animals, therefore the secondary poisoning of predators is excluded.

For use in agriculture, a technical product of zinc phosphide is marketed that contains 21% of phosphide phosphorus. When screened through a sieve with 4900 openings per cm^2, not over 20% of the substance should remain. To control gophers, poisoned baits containing 15% of zinc phosphide and 3-4% of oil are used for surface application, and containing 20% of zinc phosphide and 4-5% of oil, for aerial dispersal. To control large voles and lemmings, 10% of zinc phosphide is added to the bait; to control mice, small voles and lemmings in field conditions, and also rats in premises, baits containing 3-5% of the rodenticide are used.

In controlling gophers on pastures and the edge portions of grain fields, concentrated scattering of the bait is performed at places of

accumulation of the rodents, while around plantings, farms, water basins, and forest stands, only vertical burrows are filled with bait. The bait is oat grains used at a rate of up to 2 kg/ha plus 0.045-0.4 kg/ha of the rodenticide. The harvest time is 10 days.

To eradicate water voles on plantings of cereals, potatoes, corn, sunflowers, and grasses, a bait of wetted peas is scattered over the edge of the adjoining virgin land at the places of accumulation of the rodents, while near populated localities, farms, rivers, and at places of concentration of wild birds, it is placed under shelter with a rate of use of the bait up to 4 kg/ha, and of the rodenticide of 0.29-0.32 kg/ha. To control small mouse-like rodents in plantings of grain and grasses, in orchards, strips of forest, and on pastures, oat or wheat grains or sunflower seeds are used as bait with observance of the preceding rules; the rate of use is up to 4 kg/ha, and of the rodenticide, 0.15-0.4 kg/ha.

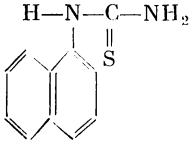
The aerial dispersal of bait is allowed only upon special permission of the USSR Ministries of Agriculture and Health.

The harvest time on plantings of grasses, corn, sunflowers, and potatoes is 15 days, and on cereal crops 10 days. The grazing of cattle is prohibited during 15 days after treatment.

The tolerance level of phosphine in cereals is 0.01 mg/kg.

Antu (Krysid)

The active ingredient is 1-naphthylthiourea:



It is a white crystalline solid melting at 198 °C. It dissolves poorly in water (600 mg/litre at room temperature) and in most organic solvents. In an alkaline medium, 1-naphthylthiourea readily decomposes to form 1-naphthylamine, which detracts from the eatability of the substance.

Antu is a stomach rodenticide. Upon entering the gastro-intestinal tract, it dissolves in the gastric juice and penetrates into the blood, sharply lowering the hemoglobin content in it. It simultaneously accelerates the sedimentation of the blood's erythrocytes two or three times.

Animals poisoned with antu die as a result of stopping of their respiration.

Rats and mice are very sensitive to this rodenticide and perish in 12-72 hours. But rats who have received a non-lethal dose of the

substance increase their resistance to it. Antu has a very bitter taste, therefore the animals develop a reflex protective reaction to it.

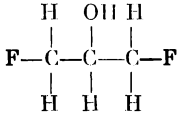
Antu is highly toxic to humans and domestic animals (LD_{50} for dogs is 130-150 mg/kg), but has no cumulative properties.

Antu is marketed in the form of a technical product of 1-naphthylthiourea finely ground to a particle size of under 0.15 mm. The fine grinding ensures rapid dissolving of the antu in the gastric juice. The formulation is used to control rodents in production premises by the method of poisoned baits. The bait material is cereal porridges with minced meat or fish; the antu content in the bait is 0.5-1%. The prolonged repeated use of antu in one building is not recommended because its effectiveness diminishes. It is necessary to alternate this substance with compounds from the group of blood anticoagulants.

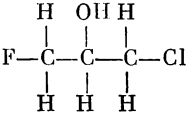
The baits are placed at the rodents' burrows, or at places accessible to livestock or poultry, in bait boxes or other sheltered places in portions of 5-10 g.

Gliftor

This rodenticide is a mixture of 1,3-difluoropropanol-2:



and 1-fluoro-3-chloropropanol-2:



The content of the first ingredient is 70-75%, and of the second one, 10-20%. Gliftor is a light yellow liquid with a specific odour. It mixes well with water and alcohol. The main ingredients of the mixture are highly volatile. The volatility of the vapours of the gliftor ingredients at 20 °C is 22.5 and 6.6 mg/m^3, respectively.

Gliftor is highly toxic to rats and mice. Upon ingestion into an animal's organism, it apparently acts on the nervous system and changes the composition of the blood. The substance does not impart an unpleasant taste or odour to bait. Animals do not develop reflex protective reactions.

A feature of gliftor is its sharply pronounced selective toxicity to rodents and birds of various species. The minimum lethal dose for rodents is 4-75 mg/kg, and for birds is 1-3 g/kg. Depending on the dose, rats perish in 2-4 days, and mice in 3-8 days.

With respect to its toxicity to humans, gliftor belongs to strong poisons with acute dermal and inhalation toxicity. It is moderately stable, with insignificant cumulative properties.

A 72% technical liquid formulation of gliftor is used on pastures and the edge parts of grass and grain plantings inhabited by gophers, at a rate of 5-10 g/ha, using oat grains as the bait. The concentration of the formulation is 0.3-0.6%; the bait is used at a rate of up to 1.6 kg/ha. The pilot use of gliftor is also permitted in plantings of cereal crops, grasses, sunflower, on haymaking fields and pastures, in orchards and forest strips inhabited by common voles and water voles at a rate of 0.015-0.024 kg/ha. The bait is wheat grains or sunflower seeds for gray voles, wetted peas for water voles. The concentration of the rodenticide is 0.4-0.6%, and the bait is used at a rate of up to 4 kg/ha.

The baits are scattered at places of accumulation of the rodents; around populated localities, farms, water basins, and forest stands it is only permitted to bait the vertical burrows of gophers or place the bait in sheltered spots. The use of gliftor is prohibited in the habitats of wild and beneficial predatory mammals.

The harvest time for plantings of grasses, sunflowers, corn, in orchards and forest strips is 20 days, and for cereal crops is 10 days.

The grazing of cattle on pastures is prohibited during 20 days.

6.2.1. Blood Anticoagulants

Among the organic substances used to control rodents, a group of compounds with an identical mechanism of action is earmarked—**blood anticoagulants.** They include derivatives of coumarin and indandione. When they are ingested into the organism of a warm-blooded animal even in small doses, the derivatives of coumarin and indandione-1,3 inhibit the process of formation of prothrombin in the organism, which is responsible for blood coagulation in hemorrhages. Simultaneously, these substances affect the capillary system of animals. As a result, the poisoned animals die because of internal hemorrhages. Virtually no protective reflex reactions are produced in animals.

Blood anticoagulants are typical chronic poisons (sharply pronounced cumulation). Their toxic action on rodents manifests itself better when ingested in very small doses (0.4-0.9 kg per animal) during several days following one another. At the same time, a single large dose does not always kill an animal. These features of anticoagulants make them unsuitable for controlling rodents in field conditions. In addition, the toxic action of blood anticoagulants is eliminated by vitamin K contained in green plants.

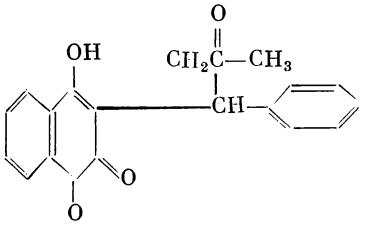
Derivatives of coumarin and indandione-1,3 are considerably less toxic to humans, animals, and birds. Consequently, blood anti-

coagulants are widely used for controlling rodents at livestock farms and granaries.

The baits are placed at the burrows, and on sections accessible to livestock or poultry, in bait boxes or other sheltered places in portions of 5-10 g.

Warfarin (Zoocoumarin)

The active ingredient is 3-(α-acetonylbenzyl)-4-hydroxycoumarin:



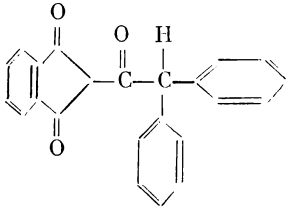
In the pure form, it is a white crystalline tasteless and odourless substance melting at 159-161 °C. It is insoluble in water, and dissolves well in acetone and dioxane, as well as in alkalies, forming the relevant derivative of the enolic form.

Warfarin is a typical zoocide with properties of a blood anticoagulant. In a dose of 4-8 mg/kg, it causes 100% perishing of gray rats. It is strongly poisonous to humans and warm-blooded animals, and has acute chronic and dermal toxicity.

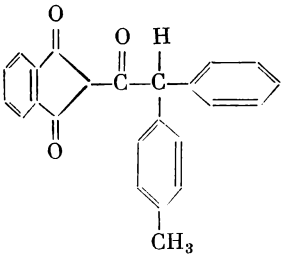
Warfarin is marketed in the form of a white powder containing 0.5% of the active ingredient, with starch used as the carrier. It is employed for controlling rodents in production premises (livestock farms, granaries) by the method of poisoned baits. The latter include bread crumbs alone or mixed with minced fish or meat. Warfarin is added in an amount of 5% of the mass of the bait. The rodents perish in 4-8 days.

Diphacinone (Diphacin, Ratindan) and Ratindan 2

The active ingredient of diphacinone is 2-diphenyl-acetyl-1,3-indandione:



and of ratindan 2 is 2-phenyltolylacetyl-1,3-indandione:



Both substances in the pure form are white crystalline powders insoluble in water. They are stable in storage and in baits. They are very close in their physical, chemical, and biological properties.

Diphacinone and ratindan 2, like warfarin, are blood anticoagulants, but have a higher toxicity to rodents, especially diphacinone (from 2 to 10 times).

For humans, they are strong poisons with acute chronic toxicity (LD_{50} for rats is 5 mg/kg). For livestock and poultry, they are moderately toxic (LD_{50} for sheep is 800 mg/kg).

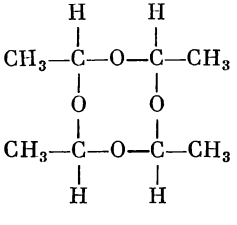
Diphacinone is marketed in the form of a bluish powder containing 0.5% of the active ingredient, corn starch being the carrier. Methylene blue imparts a light blue signal colour to the formulation. It is used to control rodents in production premises by the method of poisoned baits. Corn and wheat flour, bread crumbs, minced meat and fish, and various porridges are used as the bait material. The diphacinone is added in an amount of 3% of the bait mass.

Ratindan 2 contains 0.18% of the active ingredient. It is employed in the same way as diphacinone. It differs in having a lower toxicity to humans.

6.3. Molluscicides

Metaldehyde (Metacetaldehyde)

The active ingredient is a solid polymer of acetaldehyde:



The pure substance forms colourless flammable crystals with a mild characteristic odour. It readily sublimes, dissolves poorly in

water (200 mg/litre at 17 °C), ethanol and ethyl ether, and sparsely in benzene and hot chloroform. When heated to 50 °C in an acid medium at normal temperature, it decomposes into acetaldehyde.

In its recommended concentrations, metaldehyde has no negative effect on the crop being protected.

Metaldehyde is a contact and stomach molluscicide, highly toxic to bare slugs and snails, and has a high initial action.

It is highly toxic to humans and warm-blooded animals (LD_{50} for laboratory animals is 175-290 mg/kg), and has an inhalation toxicity. The dermal action is slight; when it gets into the eyes, it causes surface conjunctivitis. It has slight cumulative properties ($C_{cum} > 5$).

A 50% wettable powder and a 5% granulated formulation of metaldehyde are marketed. They are recommended for controlling bare slugs on grain, fruit (including citrus), technical, vegetable, and flower crops and grapevines: the former by spraying the plants and soil around them at a rate of 4-8 kg (2-4 kg a.i.) per hectare, and the granules by scattering them over the soil's surface around the plants at a rate of 15-20 kg (0.75-1 kg a.i.) per hectare on grain crops, and 30-40 kg (1.5-2 kg a.i.) per hectare on the other crops. The harvest time is 20 days. The tolerance level of metaldehyde in products is 0.7 mg/kg.

6.4. Attractants, Repellents, Chemosterilants

6.4.1. Attractants

Attractants are chemical substances whose vapours attract insects. They are divided into food attractants, substances luring insects to the place of oviposition, and sexual attractants.

The most widespread food attractants are the products of decomposition of organic matter, protein, acid, and enzymatic hydrolizates, and also molasses and various syrups. The persistence of these substances is not long (4-7 days). They are especially helpful in attracting adult specimens of apple worms, and Mediterranean and Mexican fruit flies, which is taken advantage of in predicting the appearance of pests.

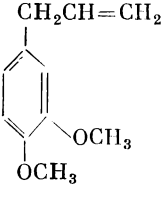
Baits are known containing dioctylphthalates, trimethylamine and piperidine, mercaptan, various fatty acids, indole, pyridine, and benzyl alcohol.

There are very few substances attracting to the place of oviposition. Insects, as a rule, oviposit at places where there is food for their progeny. Quite often, the host plants excrete attractants that can be used in principle for controlling insects. For example, substances attracting boll weevils have been separated from cotton, and an attractant for alfalfa weevils, from alfalfa.

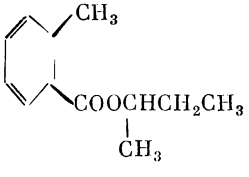
Sex attractants, which are regulators and stimulators of the reproduction processes of a species, have an exceedingly high activity, specificity, and are capable in negligible doses to attract specimens of the opposite sex over considerable distances. A female gypsy moth, emitting 10-12 mg of a substance, attracts a male from a distance of 400 m; the amount of substance emitted by one female of the pine sawfly is sufficient to attract 11 000 males from a distance of 17.5 km in five days. The high selectivity of these substances in combination with a low toxicity to mammals completely excludes the possibility of undesirable action on other components of the biocoenosis in the zone of their application.

At present, sex attractants have been discovered in *Lepidoptera*, *Hymenoptera*, *Coleoptera*, *Orthoptera*, *Hemiptera* (true bugs), *Diptera*, *Neuroptera*, termites, and scorpion flies. The separation of these substances from insects, however, requires considerable time and money. This is why natural attractants have not come into favour in agriculture.

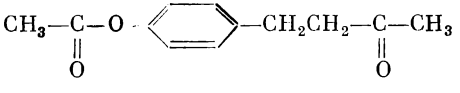
The achievements in the field of separating and identifying natural sex attractants allowed chemists to approach the stage of production of synthetic sex attractants. Already over 20 000 compounds with attracting properties have been tested. Available on the market are methyl eugenol (1-allyl-3,4-dimethoxybenzene):



attracting the eastern fruit fly, siglure:



medlure, and trimedlure for attracting the Mediterranean fruit fly, cue-lure:



an attractant for the melon fly, and some other attractants.

The employment of attractants in combination with insecticides is a promising trend in chemical plant protection. Their use elimi-

nates the need of treating large areas of agricultural lands with insecticides, which lowers the consumption of the substances, and also prevents the contamination of agricultural products and the environment with pesticide residues. The widespread introduction of sex and other attractants, however, is restricted to date because of their exceedingly narrow selectivity.

6.4.2. Repellents

Repellents, as their name implies, are chemical substances that repel insects.

Repellents can be used to protect plants against rodents, birds, insects, and mites, to protect humans and animals against parasite arthropods, and also to prevent the poisoning of beneficial insects that may occur when they visit plants treated with insecticides.

The greatest favour has been given to repellents for protecting perennial plantings against damage by mammals. The most active repellents of this group include amines, pyridine derivatives, quaternary ammonium bases, cyclic amides, and rosin. Some insecticides and fungicides also have repellent properties (for example, HCH and thiram). These substances are included in compounds for coating tree trunks and branches.

The All-Union Research Institute of Plant Protection recommends the following formulations for practical use:

rosin dissolved in denatured alcohol (1 : 1) with the addition of 50 g of naphthalene dissolved in 60 g of turpentine to one litre of the solution;

naphthalene emulsion: 1 litre of water, 0.35 kg of laundry soap, 20-40 g of naphthalene, 25-50 g of turpentine, 10 g of blue vitriol, and 0.2 litre of a vegetable oil;

a mixture containing HCH: 1 litre of water, 0.35 kg of soap, 70 g of HCH dust, and 0.1 litre of a vegetable oil.

Trees should be coated in autumn in dry weather to a height higher than the expected thickness of the snow layer. The recommended mixtures are a good means for protecting orchards against damage by rodents in winter.

Thiram, zinc phosphide, toxaphene, etc. can be used as repellents to protect plants against damage by birds.

Dimethylphthalate, dibutylphthalate, and deet (N,N-diethyl-m-toluamide) have found practical use in protecting humans and animals against insects and mites. These compounds have a strong repellent action on blood-sucking insects and mites, but their persistence is comparatively short. To protect humans and animals, repellents are used in the form of ointments, pastes, solutions, emulsions, and aerosols.

6.4.3. Chemosterilants

Chemosterilants are chemical substances that sterilize insects sexually to prevent reproduction. These substances may include chemical mutagens. The sterilizing action of a chemical may be due to the fact that (1) it damages the chromosomes and leads to the formation of dominant lethal mutations in the semen of males or mature eggs of females; (2) it causes perishing of the cells in the premeiotic stages or aspermia; (3) it inactivates the sperm, and (4) under the influence of the toxicant, females lose the ability of laying eggs. In addition, when chemosterilants penetrate into the tissues of an insect, they may damage the somatic cells, which leads to perishing of the insect. This phenomenon is extremely undesirable because the success of chemical sterilization depends on the ability of the sterile insects, especially males, to compete with the fertile specimens in the natural population.

A very important property of sterile males ensuring the success of practical sterilization of insects of the natural population is their ability of multifold mating with females. It must not be inferior to that of fertile males. Upon mating with a sterile male, a fertile female deposits non-viable eggs, thus sharply reducing the population in the next generation. The greatest effect is achieved with a ratio of sterile males to fertile males and females in the population of 3 : 1 : 1, or 5 : 1 : 1, or 10 : 1 : 1. Such a ratio is achieved by releasing males sterilized in a laboratory or by treating the natural population with chemosterilants.

Chemosterilants do not reduce the population of a pest on a given area, hence the insects may cause substantial harm to the harvest. In this connection, the effectiveness of using chemosterilants grows sharply when the size of the natural population is diminished by preliminary treatment with an insecticide or by using sexual attractants. Most chemosterilants relate to highly toxic compounds with a mutagenic, teratogenic, and cancerogenic action.

Modern chemosterilants belong to two groups differing in the mechanism of their action: antimetabolites and alkylating agents.

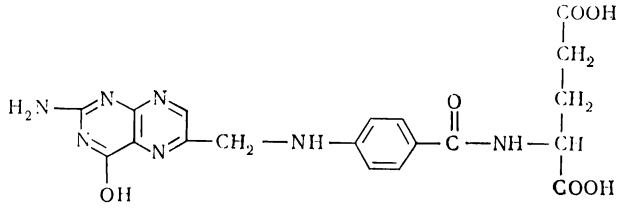
Antimetabolites are substances whose structure is very close to that of the natural metabolites of an organism. When they enter an organism, they displace these metabolites in exchange reactions. The antimetabolites of folic acid, glutamine, pyrimidine, and purine participating in the biosynthesis of nucleoproteins have the highest sterilizing activity. Upon entering an insect's organism, these substances violate the synthesis of nucleic acids (DNA and RNA) in the nuclei of the sexual cells. The effectiveness of such chemosterilants depends on the activity of the synthesizing processes in the nuclei of the cells. For instance, upon emergence from the pupae, male flies contain already mature mobile sperm, and the formation

of nucleic acids is already completed in their spermatozoids. At the same time, the rapid synthesis of nucleic acids occurs in the eggs of matured females, and the antimetabolites can exhibit their action. This explains why the chemosterilants of this group sterilize only females well.

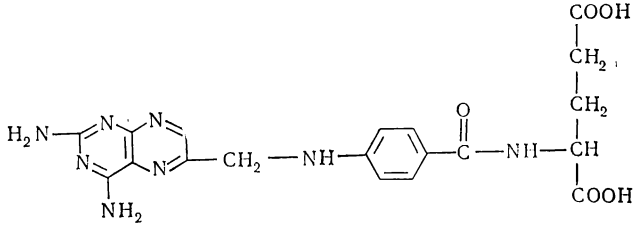
Antimetabolites mainly have stomach action and sterilize insects when ingested together with their food. These substances cause female insects to lose their ability of producing and depositing eggs. The minimum sterilizing concentration of antimetabolites in bait is 0.0025%.

Compounds of the antimetabolite group are highly toxic to humans and animals and have an embryotoxic and mutagenic action. This substantially restricts their introduction into plant protection practice.

Among the antimetabolites of folic acid, the ones studied the best are methotrexate [N-(p-(2,4-diamino-6-pteridyl)methylmethylaminobenzoyl)glutamic acid] and aminopterin [(2,4-diaminopteridyl)glutamic acid], very close in structure to folic acid:



Folic acid



Aminopterin

In a concentration of 0.05-1%, these substances caused the sterilization of up to 99.5% of house, flesh, and wine flies.

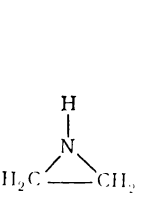
The antimetabolites of pyridine, 5-fluorouracil and 5-fluororotic acid may be used for chemical sterilization.

Alkylating substances are compounds by means of which a hydrogen atom in a molecule of a substance is substituted by an alkyl

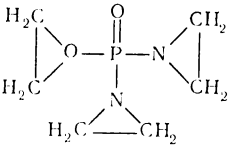
group. They readily enter into chemical alkylation reactions with various compounds of a cell, including proteins and nucleic acids. If a considerable part of a cell's molecules are involved in the reaction, the cell may perish. The dose of an alkylating agent must be selected so that most vitally important molecules will remain intact in an insect's sexual cells and thus cause sterility of the insect, while keeping it alive. In their sterilizing doses, alkylating substances act on the chromosomes, harming a DNA molecule at one or more points.

Chemosterilants of this kind have both a stomach and a contact action on insects and mainly sterilize males, causing chromosomic aberrations (breaking of the chromosomes) of the male sexual cells. This leads either to perishing of the zygote formed as a result of fertilization, or to no larvae appearing from the eggs deposited by the female.

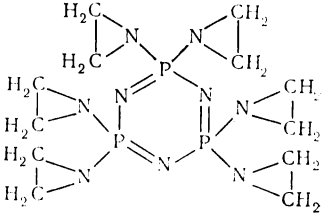
The most promising chemosterilants are derivatives of ethylene imine whose ring is a carrier of the sterilizing activity. They include tepa (aphoxide) and its methyl analogue—metepa (metaphoxide), sulphur analogue—thiotepp (sulfotepp), and also tretamine and apholate:



Ethylene imine



Tepa



Apholate

These compounds sterilize various insects and mites without reducing the sexual activity of the males. At the same time, the viability of the insects diminishes somewhat. Tretamine and thiotepp also sterilize females.

The derivatives of ethylene imine are highly toxic to humans and warm-blooded animals and have a mutagenic, teratogenic, and cancerogenic action. In some cases, the sterility of mammals was noted under the influence of the alkylating substances.

Studies performed by the All-Union Research Institute of Plant Protection have established that a 0.1% solution of thiotepp lowered the number of progeny of the turnip moth by sterilizing 85% of the males. Apholate in a concentration of its solution of 0.3-1.5% and tretamine of 0.05-0.1% had the same strong effect. These substances may be used for the sterilization of males in a laboratory and then releasing them into the environment.

The sterilization and release into the environment of sterile insects is a promising trend in plant protection. The use of chemical sterilants will reduce the scale of chemical treatments of agricultural crops, eliminate the hazard of contaminating products and the environment with poisonous pesticide residues, and exclude the negative action of toxicants on the biocoenosis. The manufacture of these substances on a large scale is being delayed owing to their unfavourable toxicological properties. The seeking of ways for the safe use of chemosterilants is going on in two directions: methods of using toxic chemosterilants are being developed that are safe for the agroecological system (for example, their use in traps with attractants), and chemosterilants are being developed that act selectively only on invertebrates and are harmless to humans and warm-blooded animals.

6.5. Fumigants

Fumigants are intended for controlling especially dangerous harmful insects, including quarantine ones, against which other pesticides have a low effectiveness. Fumigation eradicates eggs, larvae, pupae, and imagoes even in the most inaccessible places in premises and on plants, and also under wax scales impermeable to aqueous solutions. The effectiveness of fumigants is substantially influenced by the temperature of the air and the content of carbon dioxide. With elevation of the temperature, the lethal concentration of the toxicant diminishes because the intensity of respiration of the insects increases. Carbon dioxide in definite concentrations stimulates the respiratory movements and opening of the spiracles in insects, which amplifies the process of entry of a fumigant into an organism.

Sublethal concentrations of a fumigant produce a protective reaction in insects (protective stupor—parabiosis), which lowers the effectiveness of the substance. This is why the entire required amount of a fumigant must be introduced at once.

In some species of scale insects and mealybugs, the appearance of resistant races under the influence of perennial treatments with hydrogen cyanide has been noted.

The action of fumigants on a green plant, seeds, planting stock and food products varies. For example, dichloroethane has no negative effect on seeds and planting stock, but burns plants, hence it may be used only for fumigating seed grain. Methyl bromide does not burn plants, does not harm seeds and citrus fruits, and does not change the quality of many agricultural products. Some fumigants are used only for gassing empty premises (sulphurous gas).

Methyl Bromide (CH_3Br)

In the pure form, it is a colourless liquid boiling at 3.6 °C with a density of 1.732 g/cm³. It dissolves poorly in water (13.4 g/kg at 25 °C) and well in organic solvents. Liquid methyl bromide is a good solvent of fats, oils, lacquers, and varnishes, and destroys rubber, paints, and lacquer and varnish surface finishes.

The vapour of methyl bromide is heavier than air, penetrates well and deeply into sorbing materials, is poorly absorbed by them, and is readily expelled upon ventilation. An increased moisture content of agricultural products does not prevent the penetration of the vapour. In the concentrations used, a mixture of the vapour with air is not explosive.

In the chemical respect, methyl bromide is quite active. It readily enters into exchange reactions and is a strong methylating agent.

Liquid methyl bromide has a strong negative effect on green plants, planting material (burns), and seeds (lowering of germination; this influence is the stronger, the higher is the concentration of the fumigant and the moisture content of the grain). Its vapour, however, is considerably less phytotoxic. The most resistant to this fumigant are pea and sesame seeds. Barley and corn are less resistant, while wheat is the most sensitive. In the fumigation of grain, methyl bromide is sorbed physically and enters into a chemical reaction with protein substances. Here methylation of the imidazole rings of the histidine residues of methionine and lysine occurs. The fumigant has no appreciable influence on the quality of grain, however, although it does lead to a small loss in the nutritive value of bread.

In its recommended concentrations, methyl bromide does not burn vegetating plants at temperatures up to 32 °C, does not damage planting stock (cuttings, tendrils of strawberry plants), bulbs and tubers, and also fresh fruits and vegetables. The residues of the fumigant rapidly vanish from treated products, but the content of solid (inorganic) bromides in them increases.

Methyl bromide is an insecticide and acaricide with a broad spectrum of action having fumigation properties. It is highly toxic to virtually all species of harmful insects and mites and in all phases of their development. Some species of thrips and scale insects are relatively resistant to this pesticide, but they rapidly perish with an increase in the dose of the fumigant and a longer exposure. Entering an insect's organism through its respiratory tracts, methyl bromide has a toxic action mainly on the nervous system. Owing to its high methylating ability, it also reacts with enzymes containing sulphhydryl groups, upsetting oxidation-reduction processes and carbohydrate exchange. This apparently also explains the action of the fumigant on the eggs of insects and mites. The symptoms of poisoning by methyl bromide manifest themselves slowly, therefore

the effectiveness of fumigation should be determined not earlier than in 24 hours after disinfection. At a sublethal concentration of the fumigant in the air, many insects fall into a protective stupor and do not perish at a following lethal concentration.

Methyl bromide is highly toxic to humans and warm-blooded animals (LC_{50} for rats when inhaled during two hours is 2.3 mg/litre) and is a strong neurotropic poison. When ingested into an animal's organism, it violates the functions of the nervous system and changes the morphology of the blood. In its capacity of a strong methylating agent, methyl bromide has a negative effect on the processes of synthesis and decomposition of hydrocarbons. The content of glycogen in the liver diminishes especially sharply.

Methyl bromide rapidly decomposes in a mammal's organism to form methyl alcohol and subsequently formaldehyde:

$$CH_3Br + H_2O \rightarrow CH_3OH + HBr$$

$$CH_3OH + (O) \rightarrow H-\overset{\overset{H}{|}}{\underset{\underset{O}{||}}{C}}- + H_2O$$

This increases the toxic action of the fumigant still more. In large concentrations and in the liquid form, methyl bromide has a strong local abscess-forming action on the skin.

The indications of poisoning by this substance manifest themselves slowly, depending on the conditions in half an hour and more, and sometimes in two or three days.

The industry produces a technical formulation of methyl bromide in the form of a liquefied gas containing 98.5% of the active ingredient. It is recommended for fumigation in granaries with bread or fodder grain of cereal crops against insects and mites, with peas for food, fodder,or seeds against pea beetles (the rate of use is 25-35 g/m^3, the exposure is 1-2 days), for fumigation of onion and garlic in chambers against nematodes (50-60 g/m^3, exposure 4 h at 16-20 °C), seedlings of strawberries against strawberry mites (20-25 g/m^3, exposure 3 h at temperature not below 15 °C), and for the fumigation of seeds of various crops, fresh and dried fruits and vegetables, slips, sets, and other planting stock against a set of pests (30-60 g/m^3, exposure 2-4 h). Methyl bromide is widely used for the fumigation of freight in the holds of ships and in railway cars.

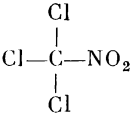
Fumigation in the USSR is performed in accordance with the "Instructions on the Disinfection with Methyl Bromide of Agricultural and Industrial Products in the Holds of Ships and of Unloaded Ships (Soviet and Foreign) against Quarantine and Other Dangerous Pests of Plants and Stored Products" (Moscow, USSR Min. of Agriculture, 1973).

To prevent damage to the planting stock, the floor of a chamber before fumigation is sprinkled with water, while slips and sets are abundantly sprayed with it. The clot of soil of sets or seedlings is also moistened to prevent harm to the root system.

All work with methyl bromide is performed by specially trained workers with the use of gas masks. No residues of the fumigant are tolerated in food products. The tolerance level of inorganic bromides in fruits is 5 mg/kg, in vegetables, dried fruits, potatoes, and fish—14, in flour—20, in grain—35, and in bread—7 mg/kg. Products may be marketed only after the completeness of degassing has been established. The maximum tolerated concentration of methyl bromide vapour in the air of the working zone is 1 mg/m^3.

Chloropicrin (Formulation 242)

The active ingredient is trichloronitromethane:



The pure substance is a colourless heavy liquid boiling at 112.4 °C. It is virtually insoluble in water (2.27 g/litre at 0 °C) and well soluble in organic solvents. Its volatility at 20 °C is 165 mg/litre. Its vapour is considerably heavier than air, is non-flammable and not explosive.

Chloropicrin vapour is sorbed to a great extent by grain, grain products, and building materials, and is slowly desorbed. At a low temperature and a high air humidity, degassing of the grain continues several months. In the passive method of fumigation, the vapour of the formulation penetrates into a grain pile in effective concentrations to a depth of 0.75 m, and into stacks of crated products up to 2 m.

At room temperature, chloropicrin vapour slowly decomposes into nitrosyl chloride and phosgene:

$$CCl_3NO_2 \rightarrow NOCl + COCl_2$$

These products hydrolyze and form substances that strongly corrode metals:

$$NOCl + H_2O \rightarrow HCl + HNO_2$$

$$2NOCl \rightarrow 2NO + Cl_2$$

$$COCl_2 + H_2O \rightarrow 2HCl + CO_2$$

Chloropicrin and the products of its decomposition are strong oxidizing agents. At an elevated temperature and air humidity, they

have a destructive action on metals, dyes, vegetable fibres, and paper.

Solutions of alkali metal sulphites decompose chloropicrin into non-toxic products; this is why they are used for decontamination of chloropicrin and containers emptied of it.

Chloropicrin vapour even in small concentrations has a strong burning effect on plants, causing their complete perishing. Fumigation of soil results in the extermination of seeds, shoots, and roots of plants. This fumigant cannot be used for disinfecting raw fruits and vegetables.

After the treatment of seed grains with chloropicrin vapour, the seed vigour and germination sharply diminish. The germination decreases most of all in the seeds of naked crops, and to a smaller extent in those of glumaceous ones; it does not change in the seeds of leguminous crops owing to the low permeability of the hulls. The change in the seed properties of grain under the action of chloropicrin vapour is explained by the disruption of the enzyme activity, first of all by the lowering of the activity of the dehydrogenases catalyzing the oxidation-reduction reactions in respiration and fermentation. The bread-baking properties of grain when gassed once with chloropicrin are retained completely. Upon the prolonged or multifold action of the fumigant, however, the strength of the gluten increases, while its unit extensibility diminishes.

Chloropicrin is an insecticide, fungicide, and bactericide with fumigation action. It is highly toxic to all species of insects and mites infecting grain, grain products, and other products of plant growing. When incorporated into the soil, the fumigant destroys nematodes, the pathogens of fungal and bacterial diseases, and the seeds of weeds.

When sublethal concentrations of chloropicrin are used, pests acquire an increased resistance to the fumigant, and resistant populations appear (for example, grain weevils). In these cases, a protective stupor of the insects may also occur.

Insects affected by chloropicrin exhibit increased respiration, decoordination of movements, and convulsions with the following paralysis. The latter, unlike protective stupor, is irreversible.

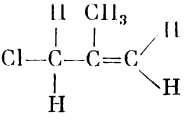
Chloropicrin with respect to its toxicity to humans and warm-blooded animals relates to the group of strong poisons. At concentrations of 20 mg/m^3 and more, acute toxic emphysema sets in. The symptoms of poisoning manifest themselves very rapidly. The fumigant does not have chronic toxicity. Chloropicrin vapour greatly irritates the mucous membranes of the eyes, causing abundant lacrimation even at non-toxic concentrations. Concentrations of only 2-2.5 mg/m^3 cause the eyelids to close in 3-20 seconds, hence it is easy to detect the presence of the fumigant vapour in premises. The liquid substance has a strong skin-irritating action.

In agriculture, a technical formulation containing 96% of the active ingredient is used. It is a heavy oily yellow liquid. Chloropicrin is recommended for the fumigation of empty storage premises and granaries against stored-grain pests at a rate of 15-40 g/m³ and with an exposure of 3-4 days, for disinfecting grain of cereal and leguminous crops to be used for food products, sunflower seeds to be processed, and seed lots of peas and fodder beans in granaries at a rate of use of 25-30 g/m³, and under canvas and synthetic films of 40-50 g/m³ with an exposure of 3-5 days. When using the passive method of fumigation, the height of piling the grain must not exceed 0.75 m, while the maximum doses are taken. The moisture content of the grain being fumigated must not exceed 16%, and the temperature of the air must be at least 12 °C. Degassing is usually performed by ventilation.

Work with chloropicrin is performed only under the supervision of a specialist, and in the USSR in accordance with the "Instructions for Controlling Pests of Stored Grain, Flour, and Cereals" (Moscow, USSR Min. of Agriculture, 1964). Marketing of the grain is allowed only after complete degassing has been ascertained. The tolerance level in grain to be processed is 2 mg/kg.

Methallyl **Chloride**

The active ingredient is 1-chloro-2-methylpropene-2:



In the pure form, it is a colourless oily liquid boiling at 72 °C, insoluble in water and well soluble in organic solvents. It is highly volatile. Methallyl chloride vapour is three times heavier than air and may ignite at concentrations of 105-339 g/m³. In practice, however, such high concentrations are not produced in the disinfection of objects.

The fumigant in the form of a vapour readily penetrates into a pile of grain to a depth of up to two metres, and physical and chemical sorption occurs. In four or five days, up to 30% of the substance combines chemically with the proteins and fats of the grain. This is why the process of degassing the seeds of some crops with a large content of these substances is protracted up to 20-30 days.

Methallyl chloride does not corrode metals and does not destroy fabrics, rubber, and other materials.

The vapour of methallyl chloride is highly toxic to vegetating plants, but does not lower the germination of seeds and does not change the quality of grain and grain products.

Methallyl chloride is a fumigating insecticide and acaricide, and is highly toxic to a broad range of stored-grain pests, including quarantine ones. In connection with the fact that it penetrates well into a grain, it is more effective than chloropicrin in controlling pea beetles, the eggs and larvae of the granary weevil.

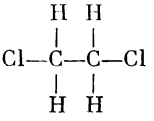
In agriculture, technical methallyl chloride is used for the fumigation of bread, fodder, and seed grain against stored-grain pests. With a height of grain piles up to two metres, the passive method of treatment is used with application of the fumigant at a rate of 50-70 g/m^3 and an exposure of three days. Grain piles above two metres high are disinfected by the active method with a rate of use of the methallyl chloride of 100 g/m^3 of grain and 30 g/m^3 of space above the grain with an exposure of three to five days.

The tolerance level of methallyl chloride residues in grain is 3.5 mg/kg. The fire safety rules must be strictly observed when working with this fumigant.

The fumigant is highly toxic to humans and warm-blooded animals when inhaled and moderately toxic when ingested into the stomach (LD_{50} for rats is 580 mg/kg). It has slight cumulative properties. The vapour of methallyl chloride irritates the mucous membranes of the respiratory tracts.

Dichloroethane (Ethylene Dichloride)

The active ingredient is 1,2-dichloroethane:



In the pure form, it is a colourless mobile liquid with a chloroform-like odour, poorly soluble in water (4.3 g/litre at room temperature) and well soluble in organic solvents; it boils at 83.7 °C.

Liquid dichloroethane dissolves well in rubber and is removed with difficulty from it.

The liquid is very volatile (300 mg/litre at 20 °C) and evaporates considerably more rapidly than chloropicrin. Dichloroethane vapour is 3.5 times heavier than air and is readily sorbed by various objects. It penetrates into piled grain to a depth of up to one metre. A mixture of the vapour with air may explode.

Dichloroethane is chemically stable and has a low activity. Like most alkane halides, however, it readily enters into exchange reactions. It is slowly hydrolyzed by water, evolving hydrogen chloride. This process is accelerated in an alkaline medium. Dichloroethane decomposes in the soil during two or three months.

The vapour of this fumigant causes major damage to green plants and planting stock (sets, slips, etc.). It has no negative effect on the quality of seed and bread grain.

Dichloroethane is an insecticide with fumigant action. It is highly toxic to soil-dwelling insects and has a prolonged persistence (2-3 months). It is inferior to other fumigants in its effectiveness against stored grain pests.

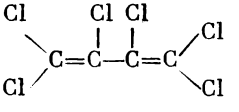
Dichloroethane is highly toxic to humans and warm-blooded animals and has pronounced dermal action; it is a strong narcotic acting on the central nervous system. Indications of poisoning are exhibited very rapidly, which makes it possible to prevent the strong poisoning of humans.

Two formulations are produced on the basis of 1,2-dichloroethane: technical dichloroethane (boiling at 74-79 °C) and distillation residues of dichloroethane with a content of 20% of the active ingredient and 60% of trichloroethylene. They are recommended for soil fumigation in vineyards against the root form of vine lice: dichloroethane at a rate of 300-500 kg, and distillation residues at a rate of 800-1200 kg/ha. The formulations are incorporated into the soil in furrows 15-20 cm deep or with the aid of a soil fumigator to a depth of 20-60 cm, not closer than 25 cm to a vine, in two periods: in spring at a soil temperature not lower than 12 °C, and in autumn after harvesting the grapes. Dichloroethane is relatively volatile, therefore after its incorporation mulching of the soil is recommended. Fumigation is performed three or four times in two years. Dichloroethane has no negative effect on the development of grapevines, and residues of the fumigant are not detected in the grapes.

The shortcomings of the given fumigants include their comparatively rapid volatilization from the soil, especially at elevated temperatures, and the high rates of use of the substances.

Hexachlorobutadiene

The active ingredient is hexachlorobutadiene-1,3:



It is a colourless liquid with an odour of camphor boiling at 216 °C. It dissolves poorly in water and well in organic solvents. Notwithstanding its high boiling point, hexachlorobutadiene has a comparatively low volatility, rate of evaporation, and diffusion. This allows it to be used as a soil fumigant.

The substance is quite inert and stable to the action of strong mineral acids and aqueous solutions of alkalies, which is why it persists for a long time in the soil.

When incorporated into the soil in doses toxic to insects, the fumigant negatively affects the root system of grapevines, causing the partial perishing of the fibrous and thin roots and preventing new root formation. The phytotoxic action of hexachlorobutadiene, however, tells only in the first year of its application. In the following years, stimulation of plant growth is observed, while the additions to the grape harvest form 20-30%. The fumigant does not affect the quality of the grapes.

6.6. Nematicides

The chemical substances employed as nematicides must penetrate well into the soil and be uniformly distributed in it, retain their activity for a long time, and have no toxic effect and aftereffect on the crops.

The persistence of nematicides is determined by the chemical properties of the substance, the rate of penetration and distribution in the soil, the physicochemical and biological properties of the soil, and the climatic conditions.

Compounds decomposing into methyl isothiocyanate (metam-sodium, dazomet), aliphatic chlorine-containing compounds (the mixture D-D, DDB), and organophosphorus compounds (heterofos) are used as nematicides.

Soil has a high absorptivity, therefore large amounts of toxicants must be incorporated into it (up to 2000 kg/ha) to produce effective concentrations.

Nematicides must be uniformly distributed over the entire tillable layer of the soil. For this purpose, liquid substances well soluble in water such as metam-sodium are incorporated with water; solid powdered formulations before incorporation into the soil are mixed with sand or soil. Nematicides can be incorporated with the aid of a GAN-8 machine or a fumigator FP-4, injectors, spilled into the furrows, or filled into holes (injections).

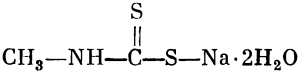
To accelerate diffusion, nematicides are incorporated by layers, and then the soil is thoroughly ploughed.

To improve the effectiveness of the incorporated nematicides evolving methyl isothiocyanate, the plots are abundantly watered.

After incorporation of the nematicides D-D and DDB, the top layer of the soil is mulched or watered with a small amount of water to form a crust 0.2 to 5 cm thick preventing the loss of the nematicides from the soil. In two or three weeks, the plots are loosened, ventilated, and seeds or seedlings are planted. Most nematicides are to a certain extent toxic to cultural plants, therefore they are used before planting or after harvesting.

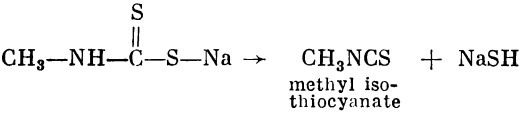
*Metam-Sodium (**Karbation, Vapam**)*

The active ingredient is sodium N-methyldithiocarbamate (the sodium salt of methyldithiocarbamic acid):



It is a white crystalline solid well soluble in water (722 g/litre at 20 °C), moderately soluble in ethanol, and insoluble in most organic solvents.

Metam-sodium is unstable and decomposes in aqueous solutions with the evolution of methyl isothiocyanate, a larger amount being evolved at lower concentrations of the solution:



For the formulation produced to be stable in storage, 0.1-1% of tertiary aliphatic amines are added to it.

Upon prolonged storage and at low temperatures, the active ingredient of metam-sodium precipitates. The precipitate can be dissolved by heating to 25-30 °C. Metam-sodium acts like a soil sterilizer, exterminating pests, including nematodes, pathogens, and weeds.

The toxic action of metam-sodium is explained by the evolution of methyl isothiocyanate that disrupts the oxidation-reduction processes in the cells of organisms. To accelerate the evolution of methyl isothiocyanate and ensure its uniform distribution, metam-sodium is greatly diluted with water (up to a 2-3% concentration) when introduced into the soil, and after its incorporation the soil is abundantly watered. The toxicant decomposes and methyl isothiocyanate is evolved. At a temperature of the soil below 12 °C, the formation of methyl isothiocyanate is retarded. The gaseous methyl isothiocyanate evolved in the decomposition of metam-sodium has an irritating effect on the skin and mucous membranes of the eyes and respiratory tracts, causing lacrimation and the secretion of mucus and sputum.

The marketed formulation of metam-sodium is a 40% aqueous solution of sodium N-methyl dithiocarbamate.

Metam-sodium is used to control root knot, potato, sugar-beet nematodes, and the stalk nematodes of onions and garlic by watering the soil with a 2% solution at a rate of 1500-2000 kg of the formulation per hectare. Metam-sodium must never be incorporated into the soil closer than one metre from trees, shrubs and other plants, nor be used in sheltered soil containing vegetating plants.

When sterilizing soil for hotbeds and greenhouses, the formulation is used at a rate of 1 kg/m^3. The soil mixture is sterilized from 30 to 50 days before its use.

To disinfect the soil and subsoil in greenhouses, a 2% solution is used at a rate of 3-10 litres per m^2, and a 1% solution at a rate of 15 litres per m^2. The heating system should be switched off not later than two or three hours before treatment.

Metam-sodium is taken in the required amount for use, is diluted with water and is incorporated into the soil with the aid of watering pots, watering pipes, liquid manure distributors, or hydraulic drills. Sprayers and atomizers must not be used because in this case the major part of the active ingredient will evaporate. The working solution is prepared directly before introduction, and only for one filling. Diluted solutions must not be stored.

In sheltered soil after the incorporation of metam-sodium, the surface layer is ploughed and compacted. After incorporation of metam-sodium into open soil, the section is abundantly watered (at least 20 litres per m^2).

The soil is disinfected almost completely during the first three days, and the metam-sodium decomposes in 5-10 days after treatment. But before setting out plants into the soil, it is necessary that the gaseous products of metam-sodium decomposition be weathered out because they are toxic to plants. To accelerate this process, the soil is ploughed twice. Usually, weathering takes 30 days.

The effectiveness of metam-sodium grows with elevation of the soil's temperature to 20 °C. At higher temperatures, metam-sodium rapidly evaporates. The ambient temperature when metam-sodium is being applied must be low (5-8 °C), therefore this is generally done early in the morning, when it is still cool.

The radius of action of the pesticide is 7.5-25 cm from the place of incorporation, but at low temperatures it drops to 2.5-5 cm.

Metam-sodium is distributed in the soil more intensively in a vertical direction.

Prior to planting vegetable plants and flowers in greenhouses, metam-sodium is incorporated into the soil not later than 30 days before planting the seeds or seedlings. On open soil fields intended for vegetables (cucumbers, tomatoes, carrots, lettuce, radish, eggplants), onions, garlic, and strawberries, metam-sodium is incorporated in the autumn at a rate of 1500-2000 kg/ha.

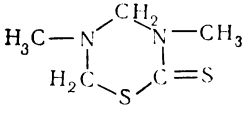
Metam-sodium is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 450 mg/kg). It has only slight chronic toxicity, and acute dermal toxicity.

Methyl isothiocyanate irritates the mucous membranes and the eyes (its LD_{50} for rats is 97 mg/kg). Dangerous concentrations of methyl isothiocyanate are created during treatment of the soil and in the first 4-7 days after treatment. To protect the respiratory organs,

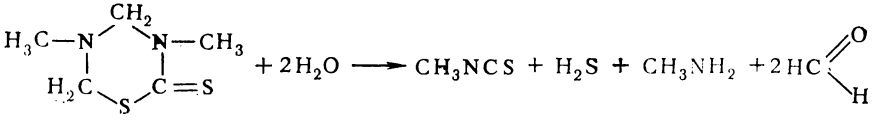
a gas mask or an antigas respirator with a cartridge "A" is needed, and to protect the skin—a rubber coated overalls, rubber boots and gloves. Reentry after treating soil greenhouses is permitted not earlier than in seven days, and after treating hydroponics greenhouses, in five days. The maximum tolerated concentration in the air of the working zone is 0.1 mg/m^3, and in the water of water basins, 0.02 mg/litre.

Dazomet (Tiazon, Mylone)

The active ingredient is tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione:



It is a crystalline substance melting at about 100 °C (with decomposition). It is poorly soluble in water (1.2 g/litre at 30 °C) and well in chloroform. When heated, in the presence of water, and in the soil, it decomposes with the formation of methyl isothiocyanate



Dazomet is employed to exterminate various pathogenic organisms in the soil. It has a complex effect with nematicidal, insecticidal, fungicidal, and herbicidal action.

It is produced in the form of an 85% powder with the addition of surfactants. Dry wood dust or other organic substances of a vegetative origin are used as the carrier because inorganic carriers catalyze the decomposition of the toxicant in storage. Dazomet is very hygroscopic, and it must therefore be stored in tightly closed containers.

The toxic action of dazomet is determined by the degree and rate of its decomposition. For this reason, it is usually incorporated into preliminarily moistened soil, and the treated field is abundantly watered (3-10 litres of water per m^2).

Prior to incorporation, dazomet is mixed with sand or screened soil in a ratio of 1 : 3 and is uniformly scattered over the surface of the field being treated with the aid of fertilizer spreaders, the soil is ploughed, abundantly watered or compacted, and covered with a polyethylene film. The radius of toxic action of dazomet is from 2.5 to 10 cm, while at a soil temperature below 12 °C it does not exceed

2.5 cm. For this reason, it is very important to ensure uniform distribution of dazomet in the soil. The process of disinfection of the soil with dazomet lasts 10 days and more. After disinfection, the soil is loosened to remove the gaseous phase.

Dazomet is used to protect vegetables in sheltered soil (cucumbers, tomatoes) by incorporating into the soil 2000 kg of the substance per hectare with its following mixing over the depth of the topsoil three or four weeks before planting. On plots earmarked for strawberries, dazomet is introduced at a rate of 1000-1500 kg/ha in autumn for spring planting or in spring for autumn planting.

To control onion nematodes, dazomet is incorporated into the soil to a depth of the topsoil at least 20 days before planting and not later than 60 days before harvesting the crop. Dazomet is applied at the same periods on plots for nematode-resistant species of potatoes at a rate of 270 kg/ha.

For quarantine purposes to eliminate seats of potato nematodes, dazomet is incorporated at a rate of 1000-2000 kg/ha in the autumn after harvesting or in the spring not later than 30 days before planting.

Dazomet is moderately toxic to warm-blooded animals (LD_{50} is 500-600 mg/kg) and has moderate cumulative properties.

The tolerance level of dazomet in food products (potatoes, cucumbers, and other vegetables) is 0.5 mg/kg.

D-D (Nemafene)

The technical product is a clear amber flammable liquid with a pungent odour containing at least 50% of *cis*- and *trans*-isomers of 1,3-dichloropropene ($CHCl=CH-CH_2Cl$), which is the main active ingredient, and 50% of 1,2-dichloropropane ($CH_3-CHCl-CH_2Cl$) and other higher trichlorides. It is virtually insoluble in water (2 g/kg at room temperature), but dissolves in organic solvents.

D-D is used for treating soil against nematodes, wireworms, cockchafer larvae and other soil-dwelling insects and certain pathogens.

It is incorporated into fields intended for spring grain crops and flax at a rate of 500 litre/ha, for nematode-resistant species of potatoes—600 litre/ha, for strawberries and currants—700 litre/ha, for beets and vegetables in open and sheltered soil at a rate of 1000-2000 litre/ha.

Treatments are performed in autumn or spring not later than 30 days before planting seeds or seedlings at a soil temperature of 10-27 °C. D-D is introduced by soil fumigators to a depth of 15-20 cm in rows at spacings of 15-20 cm. After incorporation, the soil surface is sealed by heavy rolling, or is watered until a crust forms. On small plots, the surface is covered with a film. The vapour of D-D propagates upward and horizontally over 20-25 cm from the

place of incorporation, and downward over 45 cm. The diffusion of D-D diminishes at a high moisture content of the soil. In several days prior to planting, the soil is loosened, and the evaporation of the toxicant from the soil is determined organoleptically (according to the odour).

D-D is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 840-876 mg/kg).

DDB

It is a mixture of isobutane and isobutylene dichlorides in a varying proportion. The technical product is a dark brown liquid with a pungent odour, insoluble in water.

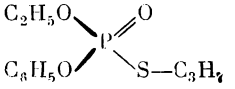
It is effective in controlling stem and root knot nematodes. Technical DDB in a dose of 200-400 kg/ha is incorporated into the soil in greenhouses 20 days before planting seeds or seedlings of vegetable crops (cucumbers, tomatoes, onions, etc.).

DDB is incorporated into warm soil with a medium moisture content, and the soil is then rolled or watered.

DDB is toxic to cultural plants, therefore it is incorporated not later than 20 days before planting the seeds or seedlings.

Heterofos (Fosthil)

The active ingredient is O-ethyl-O-phenyl-thiolpropyl phosphate:



It is a light yellow liquid with an unpleasant odour. Its volatility at 20 °C is 20 mg/m³. Its boiling point is 108-110 °C at 0.15 mmHg.

Heterofos is toxic to many species of nematodes, including root knot nematodes in sheltered and open soil, stem and cystogenous nematodes of potatoes, and also to the larvae of cereal leaf beetles, the larvae of click beetles, cabbage maggots, and the caterpillars of turnip moths.

A 7.5% granulated formulation of heterofos is recommended for pilot use on potatoes. To control cystogenous potato nematodes when planting nematode-resistant species, granulated heterofos is applied at a rate of 80 kg/ha by complete cultivation of the soil.

Heterofos is moderately toxic to warm-blooded animals and humans.

Chapter 7

FUNGICIDES

Chemicals employed to protect agricultural crops against fungal diseases are called **fungicides.** This group also includes substances effective in controlling bacterial diseases and known as **bactericides.**

Fungicides are divided into groups according to their chemical composition and structure, the nature of action on pathogens, their behaviour in a plant, method of application, and designation.

Most fungicides protect a plant by destroying the infection before entry of the pathogen, preventing infection of the plant or rendering a static action on the infection source by stopping the development and distribution of the pathogen. Only a few substances are capable of curing or healing plants by exterminating or inhibiting pathogens after infection has occurred. Depending on how fungicides act on pathogens, protective and curative fungicides are distinguished.

Protective fungicides mainly inhibit the reproductive organs of a pathogen and act on it at the place of infection before a plant is infected.

These substances are used during periods preceding the mass spreading of an infection.

Curative fungicides act on the vegetative and reproductive organs of pathogens, and also on their wintering stages, causing inhibition or perishing of the pathogen after a plant has been infected. The effectiveness of curative fungicides depends on the time that has elapsed from the instant of penetration of the pathogen into the tissues of plants to the beginning of their treatment with fungicides. The shorter this time, the higher is the effectiveness of a fungicide. The same substance in different concentrations may have either a protective or a curative effect. As a rule, substances have a curative effect when used in higher concentrations. A curative effect on plants may be rendered not only by substances acting directly on the pathogen (fungicides, bactericides), but also by substances capable of inactivating toxins or changing metabolism in plants by increasing their resistance to diseases. Such substances are said to have an immunizing (therapeutic) action.

With respect to the distribution of fungicides relative to a plant, they are divided into contact and systemic (intraplant) ones.

Contact fungicides do not penetrate into plants, but remain on their surface and act on the pathogens upon direct contact with them. This group includes most fungicides in use at present such as inorganic copper compounds, sulphur compounds, and derivatives of dithiocarbamic acid.

Contact fungicides may have a local penetrating effect, permeating deep into a seed and destroying an infection that has just come into

the outer shells of seeds (thiram and other substances have such an effect).

The persistence of contact fungicides is determined by the time they spend on the surface of plants in effective amounts and depends greatly on the meteorological conditions.

Systemic fungicides are compounds or their decomposition products that are assimilated by a plant, transported in it (from the roots to leaves, from old leaves to young ones, etc.) and in concentrations not causing harm to the plant prevent the infection of the entire plant or exterminate the pathogens that have already penetrated into it. This group includes a number of synthesized and tested substances effective in controlling diseases whose pathogens develop within plants. The persistence of systemic fungicides depends to a smaller extent on the meteorological conditions and is mainly determined by the rate and nature of their metabolism.

The **way of using (appointing) fungicides** is determined by the nature of their action on the plant being protected and the pathogens, their physicochemical properties, and also by the features of infection (the source, spreading, intactness). Depending on their application, fungicides are divided into seed protectants, soil-treating substances, fungicides for treating dormant plants (eradication spraying), and fungicides for treating vegetating plants.

Seed protectants are chemical substances used to protect plants from diseases by treating their seeds. They are employed to control diseases whose source of infection is spread by seeds or is in the soil.

Soil-treating fungicides are chemicals used for incorporation into the soil to disinfect it from harmful microorganisms. Soil disinfection is especially essential and effective in greenhouses and hotbeds. Substances with a relatively high volatility and acting in the form of gases or vapours are introduced into the soil.

Fungicides for treating dormant plants are chemical substances having a contact eradicating effect that exterminate wintering stages of pathogens and pests. They harm green plants, therefore they are used in the early spring (before opening of the buds) and late autumn or in winter.

Fungicides for treating vegetating plants are chemical compounds used in the period of plant growth and development. Most of them are characterized by a protective action and are used before plants are infected, preventing this, or soon after infection, preventing development of the disease.

7.1. Selectivity and Specificity of Action

By the **selectivity** of fungicide action is meant the ability of a fungicide to inhibit parasite microorganisms without damaging cultural plants, and its different toxicity to microorganisms.

Non-selective fungicides are substances killing pathogens differing in their nature, but also toxic to plants. They are customarily used in the early spring (before opening of the buds) or are incorporated into the soil long before planting (DNOC, nitrafen, metam-sodium). It must be noted that many selective fungicides in increased concentrations may also exhibit phytotoxicity in definite conditions (formulations of copper or sulphur).

The biochemical foundation of the vital processes in higher plants and in lower ones, which fungi and bacteria belong to, is similar in many aspects, but there are nevertheless substantial distinctions between them that are just what underlies the selective action of fungicides.

The outer coats of most fungi contain the polymer acetyl-glucosamine. The main structural material of a plant is cellulose. For this reason, chemical substances disrupting the formation of acetylglucosamine play the role of selective fungicides. For example, the antibiotic griseofulvin inhibits the development of the tips of the hyphae, preventing the synthesis or inclusion of acetylglucosamine into the cell walls of a fungus, and the fungicide quintozene appreciably lowers the content of hexosamine in the walls of the mycellia of the fungus *Neurospora crassa.*

Some fungicides belonging to the group of sulphonamides are effective only against obligate parasites tendering specific demands to their food and, consequently, more susceptible to antimetabolites than their host.

The enzyme systems of fungi and higher plants have many common properties. This explains why some fungicides inhibit the enzyme systems of both a parasite and a cultural plant to the same extent. The selectivity of such fungicides is based on their ability to accumulate in the tissues of fungi in much larger amounts than in the tissues of plants. This is due to the differences between the lipids of the external tissues of fungi and plants. The waxy coat on the epidermal cells of plant leaves, the external hulls of seeds, and the covers of plant roots protect them against the penetration of foreign chemical substances. For instance, the uredospores of the pathogen of bean rust absorb five times more sulphur than bean leaves.

The effect of fungicides varies with respect to different species and even varieties of plants. For example, copper fungicides are more toxic to apple trees and less toxic to potato haulms.

By the **specificity** of fungicide action is meant the differences in their effect on microorganisms. Some fungicides display toxicity only with respect to separate species of pathogens, whereas others have a broad spectrum of action and are effective against many pathogens. For instance, copper formulations are mainly effective against downy mildews, hexachlorobenzene is only effective against covered smut and dwarf bunt, whereas dichlofluanid is effective in controlling

engenic decay of grapes, mildew and oidium of grapes, and also apple scab.

The specificity of fungicide action is associated with the difference in the absorption, accumulation, and detoxification of the fungicides.

For example, carboxin is rapidly absorbed by sensitive fungi and in insignificant amounts by resistant ones.

As a rule, the resistance of individual fungi to fungicides is explained by the impermeability of the walls of their mycelia to a fungicide or by their ability to rapidly detoxify the fungicide.

The detoxification of fungicides is often due to their reaction with the sulphhydril groups in cells. For instance, *Aspergillus niger*, distinguished by its high thiol content, is more resistant to mercury formulations than *Rhisoctonia solani* and *Pythium ultimun.*

7.2. Biological Fundamentals of Use

All plant diseases, depending on what causes them, are either non-infectional or infectional.

Non-infectional diseases of plants cannot be transmitted from one plant to another and are caused by unfavourable soil and climatic conditions, abnormal nutrition, the action of harmful chemicals, radiation, improper farming practices, and mechanical damage to plants.

Infectional diseases are caused by lower non-chlorophyllaceous organisms—fungi, bacteria, and also by the most minute mycoplasmic organisms and particles of living protein substance—viruses.

Chemical measures in controlling diseases caused by mycoplasmic organisms and viruses to date have a very limited use (the dressing of seeds with potassium permanganate, the inactivation of viruses by the salts of some metals and organic acids, and the increase in the resistance to viruses of plants treated with antibiotics).

Fungicides are mainly used to protect plants against infectional diseases caused by fungi and bacteria.

Fungal and bacterial infections mainly spread via the air by means of the wind, rain, by insects, and by humans when caring for the plants. Most parasites penetrate into plants through the natural openings in vegetative tissues (stomas, water pores, nectar glands, cracks in bark, eyes of potatoes), and through openings caused by mechanical damage to the vegetative tissues.

Parasites also exist that penetrate into a plant directly through its epidermis. An example are the pathogens of powdery mildews (Fig. 13). When they get onto a plant, the spores of these fungi sprout, and drill the cuticle with their shoots, incorporate themselves into a tissue, ensuring nutrition and remaining on the damaged surface. The fungus in this case develops on the surface of a plant (exoparasite). In the majority of cases, however, the infectional source,

getting into a plant, develops inside it, occupying either intercellular spaces or a cell (endoparasite). Typical endoparasites are the pathogens of cabbage keel, potato cancer, and downy mildews. The development of parasites inside plants hampers their eradica-

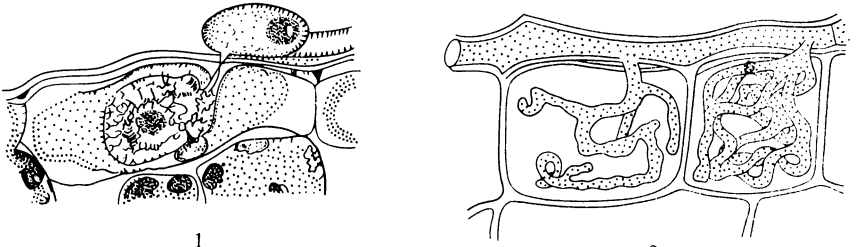


Fig. 13. Haustoria of powdery mildew (*1*) and downy mildew (*2*) fungus in plant cells (after M. Dementyeva)

tion. This is why the protective measures used are most often aimed at preventing the infection of plants, and not at destroying the pathogens.

The selection of fungicides for controlling plant diseases is based on the features of development of the plants, their infectability by diseases, the nature of the infection, and the nature of action of the fungicides.

The main purpose of the chemical method of controlling diseases is to prevent plant diseases. One of the sources of diseases of annual crops (grain and technical) is infected planting stock. This is why the disinfection of seeds acquires paramount importance. The treatment of seeds with combined disinfectants in good time is especially effective. The proper use of disinfectants reduces the number or completely eradicates the activity of the harmful organisms at the beginning of their development and makes it possible to avoid treatment with fungicides or diminish it during the vegetative period of plants.

Annual crops planted by seedlings require disinfection of the greenhouse or hotbed soil in addition to seed dressing. This ensures the obtaining of healthy seedlings and prevents the infection of the open soil plots.

In the growing of perennial crops (fruit trees, berries, grapevines), of great importance is the inhibiting of the infection source remaining on green parts, plant residues, and on the soil's surface. The inhibition of the wintering stage of a pathogen prevents the infection of plants at the initial stages of ontogenesis and ensures their active growth at the beginning of vegetation.

During the vegetation period, preference is given to fungicides having a protective action. The proper fungicides or mixtures of them must be selected with a view to the prevailing diseases jeopardizing the harvest. The best result is often obtained by alternating treatments with different fungicides. Toxicants with an eradicating action are more effective in controlling powdery mildew fungi. The comparatively short period of persistence of fungicides on the surface of green plants, the constant growth of new vegetative organs, and the appearance of new infection make repeated treatments necessary during the entire vegetation period. But the perennial spraying of plants with the same fungicides may lead to the appearance of resistance of phytopathogenic organisms to these substances. Hence, to prevent a reduction in the effectiveness of treatments, fungicides from different groups as regards their chemical structure must be alternated.

To avoid the accumulation of fungicide residues in the harvest, it is necessary to strictly observe the recommended rates of use of pesticides and the harvest time, i.e. the time that must elapse after the last treatment with a pesticide before the crop may be harvested.

7.3. Fungicides for Plant Treatment during Vegetation

Fungicides used during vegetation protect different parts of plants against fungi and bacteria.

With respect to the nature of their action, their behaviour in plants, and their fungicidal properties, they can be divided into several groups (Table 13).

1. Contact formulations with a protective action effective against pathogens such as downy mildew (grape mildew, late blight of potatoes and tomatoes, blue mould of tobacco and sugar beets, etc.). This group includes inorganic copper compounds, derivatives of dithiocarbamic and phthalic acids, and dithianon.

2. Contact formulations with a protective and curative action effective against diseases caused by powdery mildew. These fungi have an external mycelium and can be suppressed (oidium of grapes, American powdery mildew of gooseberries, powdery mildew of apples, cucumbers, etc.). This group includes compounds of inorganic sulphur, nitroderivatives of phenol, and also formulations of other groups of chemical structure: FDN and quinomethionate. All these substances, characterized by an acaricidal action, are effective in controlling scab and blight. EPTC is a fungicide with a broad spectrum of action and is also effective in controlling gray mould and grape mildew. The fungicides dodine and anilat are narrowly specialized: the former is used to control apple scab, and the latter, the rust of grain crops.

Table 13. Classification of Fungicides Used for Treating Vegetating Plants

Behaviour in plants, nature of action	Group according to chemical structure	Fungicides	Disease
Contact, protective action	Copper-containing substances	Bordeaux mixture, copper oxychloride, copper naphthenates	Diseases caused by downy mildew fungi (grape mildew, late blight of potatoes and tomatoes, blue mould of onions, tobacco, etc.), spot of stone fruits, apple and pear scab, etc.
	Derivatives of dithiocarbamic acid (DTCA)	Zineb, metiram, cuprozin-1, polymarzin, mancozeb	
	Mixture of copper-containing fungicides and derivatives of DTCA	Cuprosan, miltox special, polychom	
	Derivatives of phthalic acid	Captan, folpet	
	Substances of various groups	Dithianon	Apple and pear scab, grape mildew
Contact, protective and curative action	Formulations of inorganic sulphur	Ground sulphur, colloidal sulphur, lime sulphur	Diseases caused by powdery mildew, apple and pear scab
	Nitroderivatives of phenol	Dinobuton, dinocap	
		Binapacryl	Powdery mildew of apples and pears
	Substances of various groups	Quinomethionate	Powdery mildew of apple, pear, and grapevine seedlings and sets
		FDN, EPTC	Oidium, gray rot and mildew of grapes, gray rot of strawberries, powdery mildew of cucumbers
		Dodine	Apple and pear scab
		Anilat	Brown rust of wheat
Systemic fungicides	Derivatives of benzimidazole	Benomyl, carbendazim, thiophanate-methyl	Diseases caused by powdery mildew, apple and pear scab, spot of stone fruits, brown rust of wheat, etc., except diseases caused by downy mildew
	Substances of various groups	Pyrazophos, IBP	Powdery mildew, rice pyriculariosis

3. Systemic formulations relating in their chemical structure to different groups. The greatest favour in practical work has been found by benzimidazole derivatives (benomyl, carbendazim, etc.), and also thiaphanate methyl and pyrazophos. They are toxic to many pathogens except phycomycetes. The phosphorothioic acid derivative IBP is effective against rice pyriculiariosis.

One of the features of using fungicides on vegetating plants is the plurality of treatments (from two to six). The reason is that most of the substances used are characterized by a low persistence, which is determined by the retaining of the toxicant on the treated surface in fungicidal doses and usually ranges from 5 to 25 days. Consequently, to ensure reliable protection of plants in the vegetation period, fungicide treatments must be repeated every 5 to 25 days. A major role is played by the proper choice of the treatment time. As a rule, treatment with protective fungicides must precede the infection of plants, preventing it, or must be performed soon after infection, preventing the spreading of the disease.

The effectiveness and reliability of protection are determined by how uniformly a fungicide covers the different parts of plants. All the leaves of plants, both outside and inside the crown, must be uniformly coated with the formulation. Dripping of the working liquid from leaves must never be tolerated.

The thoroughness of treatments is achieved by the use of modern equipment, low-volume spraying, and by the proper choice of the rates of use of the working liquid.

Unlike contact fungicides, the duration of whose protective effect is determined by how long they remain on the surface of foliage, systemic formulations penetrate into plants, move in and intoxicate plants, inhibiting the development of a fungus's mycelium inside a plant. They are distinguished by their longer persistence, more uniform distribution over a plant, and their effectiveness depends to a smaller extent on the amount of atmospheric precipitation falling after a treatment.

7.4. Copper-Containing Compounds

Among the copper-containing compounds, copper oxychloride and Bordeaux mixture are in the greatest favour for treating vegetating plants. Copper naphthenates are used to a limited extent.

Copper compounds are contact protective fungicides. They have a stronger effect on the germination of spores than on the growth and development of the mycelium of fungi.

The fungicidal action of copper-containing compounds is associated with the adsorptivity of the cytoplasm of the cells of fungi.

Although copper formulations (except for blue vitriol) are poorly soluble in water, a solution always contains a certain amount of

copper ions. The spores of fungi, adsorbing the copper from the solution, disturb equilibrium, and as a result a new portion of copper dissolves and is absorbed by the spores. The dissolving of the copper is facilitated by substances evolved by plants, fungi, by the carbon dioxide in the air, and by rainfall.

The intensive transition to a water-soluble state increases the fungicidal action of copper fungicides, but simultaneously also intensifies their toxic effect on plants.

The spores gradually adsorb copper up to lethal doses. The toxicity of copper compounds is due to their ability to precipitate proteins, which causes the coagulation of cytoplasm. Copper reacts with the sulphhydril groups of enzymes and coenzymes, with the amino-groups of acids and other compounds.

The effectiveness of copper-containing fungicides is determined by the uniformity, thoroughness, and opportuneness of treatment. Copper compounds are effective against downy mildew, late blight, blue mould, apple and pear scab, and certain spots and blotches. The mycelium of the pathogens of these diseases develops inside the tissues, and it is impossible to exterminate it by using contact fungicides. Hence, the main way of protecting plants from these diseases is to prevent infection. Copper formulations must be applied to plants in good time, before a disease develops. This is the aim of what we call reserve or blue spraying with Bordeaux mixture and of the regular treatment of plants with protective fungicides during their vegetation. The duration of the protective action of inorganic copper compounds is determined by their persistence on the treated surface and ranges from 10 to 20 days.

One of the shortcomings of copper formulations is their phytotoxicity, which comes to the forefront especially in years with an increased humidity of the air and a prolonged period of rainfall. In the same conditions, different species and even different varieties of plants differ in their sensitivity to copper-containing formulations.

Since phytotoxicity manifests itself to a greater extent during the period of active growth of plants, it is recommended to alternate treatments with copper-containing and with organic fungicides. Before and during blossoming, organic formulations should be used because they are safe to the flowers and stimulate the growth of leaves and shoots. Copper oxychloride is used closer to ripening of the fruits. It is less phytotoxic than Bordeaux mixture, but it is retained more poorly on plants. The standard nature of copper oxychloride and the simplicity of using it makes it a good substitute for Bordeaux mixture.

Copper compounds are stable and can circulate in the environment, therefore their use leads to an increase in the copper content in plants, the soil, and water basins.

Copper and its compounds have a fungicidal and bactericidal action on the microorganisms in the soil and water basins, disrupting the processes of mineralization of organic substances.

Notwithstanding the circumstance that copper is a microelement having a widespread occurrence in nature, its formulations are poisonous to humans and warm-blooded animals. Doses of copper salts of 0.2-0.5 g caused vomiting, and 1-2 g—lethal cases of poisoning. These salts are strong irritants of the mucous membranes of the gastro-intestinal and upper respiratory tracts and may have a local irritating effect on the skin (rash with itching, eczema).

When working with copper-containing formulations, one must use individual means for protection of the skin and eyes, and anti-dust respirators.

To prevent the accumulation of copper formulations, the harvest time is established equal to 15-20 days. The maximum tolerated concentration of copper in the air of the working zone is 1 mg/m^3, in water basins, 0.1 mg/litre, and the tolerance level in fruits is 5 mg/kg.

Bordeaux Mixture

It consists of basic copper sulphate with an admixture of gypsum. It is prepared from copper sulphate and hydrated lime. The quality of the mixture depends on the concentration of the solutions of copper sulphate and lime milk taken for its preparation, and also on the way of mixing. It is important that the copper sulphate react with the lime in an alkaline medium. In this case, mainly finely dispersed particles (3-4 μm) of basic copper sulphate are formed:

$$4CuSO_4 + 3Ca(OH)_2 = CuSO_4 \cdot 3Cu(OH)_2 + 3CaSO_4$$

Such a suspension is sufficiently stable, has a good adhesiveness and tenacity on the surface of plants, and a high fungicidal activity.

Bordeaux mixture is used in concentrations of 1-4% at a rate of from 600 to 1200 litre/ha (the copper sulphate is used at a rate of 6-60 kg/ha).

The concentration of a working solution of Bordeaux mixture is determined by the amount of copper sulphate used for its preparation.

Bordeaux mixture is prepared directly prior to use and only in the required concentration. The prepared mixture should never be diluted with water because the result will be rapid stratification. Upon prolonged storage, aggregation of the mixture particles occurs, which causes them to precipitate and adhere poorly to plants.

On the basis of the above reaction equation, the ratio of the copper sulphate to the lime in preparing Bordeaux mixture should be 4:3.

In practice, however, the two substances are usually taken in the ratio of 1:1 (because of the insufficiently high quality of the lime).

To prepare 100 litres of 1% Bordeaux mixture, one must take 1 kg of copper sulphate, dissolve it in 50 litres of water, slake 1 kg of lime in a small amount of water, and then add water up to 50 litres. The copper sulphate solution is then slowly poured with stirring into the lime milk. Should the lime milk be poured into the copper sulphate solution, the reaction proceeds in an acid medium, and larger particles form in the suspension that rapidly precipitate and are characterized by a poorer adhesiveness and tenacity on the treated surface. When hot mixtures of copper sulphate and lime are mixed, the resulting Bordeaux mixture will also have a poor quality because large, rapidly settling particles are formed. Bordeaux mixture must never be prepared in a vessel made from corrosive dematerials.

After preparing Bordeaux mixture, one must check its reaction (blue litmus test paper must not change its colour, and an iron object must not become coated with copper). Bordeaux mixture with an acid reaction is neutralized with lime milk. It may not be mixed with organophosphorus insecticides and other formulations that decompose in an alkaline medium.

The fungicidal action of Bordeaux mixture is due to the fact that upon hydrolysis under the influence of the carbon dioxide contained in the air, and evolved by fungi and plants, the basic salt of copper sulphate decomposes and liberates small amounts of copper sulphate:

$$CuSO_4 \cdot 3Cu(OH)_2 + H_2O + 3CO_2 = CuSO_4 + 3CuCO_3 + 4H_2O$$

If this process occurs intensively (at a high humidity and temperature), the protective action of the Bordeaux mixture will be brief, and damage to the plants is possible.

The effectiveness of Bordeaux mixture depends on when it is applied. The best results are obtained from treatments not long before infection, but this is possible only with accurate forecasting. To set up a reliable barrier to infection, in the early spring (during the period of bud swelling or at the beginning of bud opening), reserve (blue) spraying of orchards and grapevines is performedtare). 3-4% Bordeaux mixture (30-60 kg of copper sulphate per hec with This treatment is usually effective against scab and brown rot, clusterosporiosis of stone fruits, and red spot of plums.

For summer treatment, Bordeaux mixture with a concentration of 1% (6-20 kg of copper sulphate per hectare) is used with intervals of 7-15 days between treatments.

Bordeaux mixture that has been properly prepared and applied in favourable conditions is effective against many diseases and can be used to treat fruit, including citrus, berry crops, grapevines, potatoes, tomatoes, cucumbers, canteloupes, beets, onions, hops, alfal-

Table 14. Application of Bordeaux Mixture

Crop	Disease	Time of first treatment
Alfalfa	Brown leaf spot	When disease appears
Apples	Moniliosis (brown rot)	Before blossoming
	Scab, apple-tree cancer, rust	Blue spraying
Apricots	Clusterosporiosis (reddish brown spot), curliness	Before budding
	Coccomycosis	In the flower budding stage
Beans	Anthracnose	In seed-leaf stage
Cabbage	Downy mildew, black spot (alternaria leaf spot), phomosis, wire stem	When disease appears
Cherries	Witches' broom	Before budding
	Clusterosporiosis, moniliosis (brown spot)	Blue spraying
	Coccomycosis	Before blossoming
Citrus fruits	Anthracnose, bacterial blight, wart (scab), malesecco	Before blossoming, immediately after spring trimming
Cucumbers	Anthracnose, bacteriosis, downy mildew	At first symptoms of disease
Gooseberries and currants	Anthracnose, rust	Before or during budding
Grapes	Anthracnose, mildew, black rot	Ditto
Onions	Blue mould, rot rust	Before or upon appearance of first symptoms of disease
Peaches	Clusterosporiosis, leaf curliness, moniliosis (brown rot)	Blue spraying
Pears	Leaf spot, scab	When flower buds become pink
	White leaf spot	After blossoming
	Pear-tree cancer	Blue spraying
	Rust	Upon budding
Peas	Ascochyta leaf spot	Before blossoming
Plums	Pockets, clusterosporiosis, moniliosis (brown rot)	Blue spraying
	Coccomycosis	In the flower budding stage
	Red spot	Upon swelling of the buds
Potatoes	Macrosporiosis and phytophthora	When disease appears
Raspberries	Anthracnose, white leaf spot (septoria spot) and purple leaf spot	At length of young shoots of 15-20 cm
Soybeans	Cercosporosis	At first symptoms of disease
Strawberries	White and brown spot	Before budding
Sugar beets	Cercosporosis, rust	At first symptoms of disease

Table 14 (*concluded*)

Crop	Disease	Time of first treatment
Tobacco	Bacterial wildfire	At first symptoms of disease
	Black root rot	Watering of soil in nurseries
Tomatoes	Macrosporiosis	When disease appears or before planting seedlings into soil
	White spot (septoria spot) and late blight	When disease appears or upon first infructescence
	Black bacterial spot	When disease appears or in two weeks after planting seedlings into soil
Watermelons, canteloupes	Anthracnose and ascochyta leaf spot	At first symptoms of disease

fa, and medicinal plants (Table 14). Bordeaux mixture is not effective with respect to powdery mildew diseases, and also to blue mould of tobacco.

The harvest time for most crops is 15 days, for melons is 5 days, and for tomatoes, 8 days, provided that thorough watering is performed in harvesting.

Bordeaux mixture as regards its adhesiveness and tenacity on plants occupies the first place among the protective fungicides. But in connection with the large consumption of copper sulphate, the difficulty of preparation, and also with the possibility of damaging plants, this fungicide is being replaced with copper oxychloride and organic fungicides.

Bordeaux mixture is only slightly toxic to humans and warm-blooded animals. The tolerance level in fruits and vegetables is 5 mg/kg, and in meat and eggs is 2 mg/kg (reduced to copper sulphate).

The maximum tolerated concentration in the air of the working zone is 0.3 mg/m^3, and in water basins is 0.1 mg/litre.

Copper Oxychloride

This substance is a basic salt of copper chloride [$3Cu(OH)_2 \times \times CuCl_2 \cdot H_2O$]. It is a solid crystalline substance insoluble in water and organic solvents. It is stable to sunlight, moisture, and an elevated temperature, but is decomposed by alkalies. It is marketed in the form of a 90% wettable powder of a bluish-green colour, without an odour.

Copper oxychloride is used to treat apple, pear, plum, peach, cherry, and apricot trees, grapevines, potatoes, tomatoes, sugar

beets, cucumbers, onions, and hops against the same diseases as Bordeaux mixture. In practice, their effectiveness is the same. Copper oxychloride has a lower tenacity on plants, but its phytotoxic effect is slighter than that of Bordeaux mixture. A substantial advantage of copper oxychloride is its constant composition and the simplicity of preparing the working compositions.

Copper oxychloride is used for spraying plants during their vegetating period in a 0.4% suspension, at a rate of 2.2-8 kg/ha. For the low-volume aerial spraying of sugar beets, a 90% wettable powder of copper oxychloride is used with the addition of a 93% emulsifiable concentrate of the antivaporizer AI-4P. The low-volume aerial spraying of beets is performed during the vegetating period with an 8% and 16% suspension. The rates of use of the copper oxychloride and the antivaporizer are 4 and 0.13-0.25 kg/ha, respectively. The antivaporizer diminishes the losses of the pesticide by 40-60%, and increases the density of covering the surface of the treated plants from 1.5 to 2 times.

Copper oxychloride may cause burning of the leaves and harm to fruits in crops sensitive to copper-containing formulations and in conditions of sufficient moisture. This is why its use must be differentiated depending on the zone and the crop: in zones with a dry summer, copper oxychloride produces a high effect, whereas in regions with adequate moisture it is better to use organic fungicides. The danger of damaging plants diminishes when copper oxychloride is used in combination with organic fungicides from the group of dithiocarbamates (zineb, metiram). In such a mixture, the organic compounds are distinguished by a high persistence and are more toxic to pathogens (see cuprosan, miltox special, and polychom on following pages).

Copper oxychloride is moderately toxic to humans and warm-blooded animals (LD_{50} for mice is 470 mg/kg). When ingested into an organism, it may cause inflammation of the gastro-intestinal tract. It has moderate cumulative properties.

To prevent the accumulation of copper oxychloride residues in food products, a harvest time of 20 days must be adhered to.

Copper Naphthenates (CNC, Kupronaft, Cuprinol)

These are a dark green viscous oily paste insoluble in water, but well soluble in mineral oils when heated.

Copper naphthenates are marketed in the form of a 50% paste that produces an emulsion when mixed with water. It is highly stable in storage.

The formulation is used to control scab, brown rot of apples and pears, mildew and anthracnose of grapevines. Spraying is performed during the vegetation period at a rate of 12-22 kg/ha.

Copper naphthenates have a burning action on the plants being protected, which restricts their use.

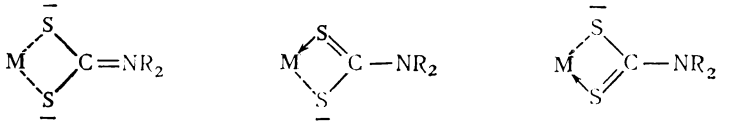
Copper naphthenates are only slightly toxic to humans and warm-blooded animals (LD_{50} for mice is 1100 mg/kg). The harvest time for orchards and grapevines is 20 days. The tolerance level in grapes is 4 mg/kg.

7.5. Dithiocarbamic Acid Derivatives

Among the derivatives of dithiocarbamic acid, the zinc, copper, and manganese salts of ethylenebisdithiocarbamic acid are used to protect plants during their vegetation period.

To extend the spectrum of fungicidal action, formulations are manufactured that contain various salts of ethylenebisdithiocarbamic acid (for instance, cuprozin-1 contains zinc and copper salts).

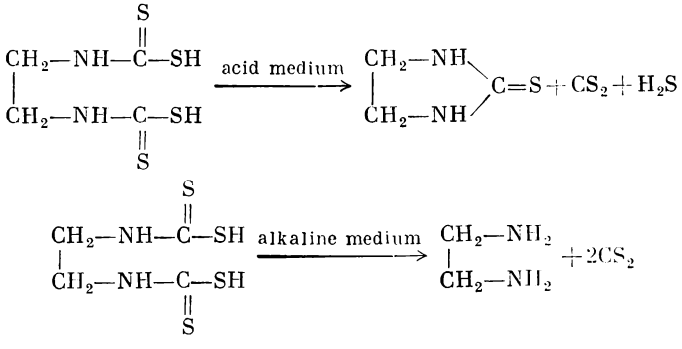
Dithiocarbamic acid and its derivatives are typical chelating agents. Owing to the presence of the group R_2NCS_2, they readily enter into a reaction with metals (M):



It has been established that when zineb is used with thiuram disulphides, intensification of the fungicidal properties occurs, probably due to the chelation (complex formation) of the zinc.

Polymarzin contains zinc and manganese salts of ethylenebisthiocarbamic acid combined with ethylenethiuram disulphide, while metiram contains zinc ethylenebisdithiocarbamate together with ethylenebisthiuram polysulphide. Hydrolysis of the salts leads to the formation of an acid.

Free ethylenebisdithiocarbamic acid is not stable and rapidly decomposes in an acid medium to ethylenethiourea, and in an alkaline medium to ethyleneamine:



Dithiocarbamic acid derivatives are contact fungicides with a protective action and are most effective when used directly prior to infection or immediately after it.

Dithiocarbamic acid derivatives have a slight genostatic action, but inhibit the vital activity of fungi and microorganisms, blocking the activity of their enzymes. It is assumed that dithiocarbamates and thiuram sulphides in microorganisms and plants decompose to the ion of dithiocarbamate acid, which reacts with the metals or thiolo groups of the enzymes.

Ethylenebisdithiocarbamic acid derivatives in the environment decompose during 1-1.5 months. It is important to note that complex ethylenebisdithiocarbamates such as metiram and polymarzin are more stable and decompose at a slower rate than zineb. The salts of ethylenebisdithiocarbamic acid, as a rule, are retained on the surface of plants without penetrating into their tissues. They disappear as a result of being washed off the plants and decomposing under the influence of abiotic factors. The heat treatment of food products leads to the decomposition of the residues of these substances.

The transformation of dithiocarbamic acid derivatives results in the formation of volatile compounds such as carbon disulphide, hydrogen sulphide, and dimethylamine, as well as the comparatively stable ethylenethiourea and ethylenethiuram disulphide, which are detected in food products, soil, and water.

The decomposition products are toxic, and some of them, particularly ethylenethiourea, are more dangerous than the initial substances. In natural conditions, however, when the recommended amounts of the formulations are used, ethylenethiourea is formed in small amounts and undergoes photolytic decomposition.

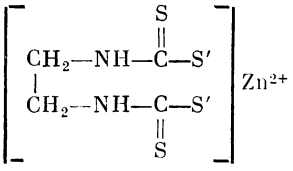
Ethylenebisdithiocarbamic acid derivatives are only slightly toxic to humans and warm-blooded animals, with a moderate and slight cumulative and slight blastomogenic action.

The advantage of dithiocarbamic acid derivatives over inorganic fungicides of the copper group is their low phytotoxicity. They positively affect the growth and development of plants, which explains why they are usually recommended for use in the period of intensive growth (in spring and the early summer). To prevent the accumulation of dithiocarbamic acid derivatives and their decomposition products in plants, the harvest time for them is 8-20 days.

The most important members of this qroup of fungicides are described on the following pages.

*Zineb (**Dithane Z-78**)*

The active ingredient is zinc ethylenebisdithiocarbamate:



It is a yellow powder with a disagreeable odour, dissolves poorly in water (10 mg/litre at room temperature) and in organic solvents, dissolves moderately in pyridine. It is not volatile. It decomposes in an acid medium to form carbon disulphide.

Zineb decomposes when heated (before melting), has a low stability in the presence of moisture and light, and when stored in poor conditions it decomposes by 50% during a year.

To prevent its decomposition with the liberation of the explosive carbon disulphide, it is recommended to store zineb on racks in well ventilated premises at a low temperature.

In biological media, zineb decomposes during a month, while the toxic products of its transformation (ethylenethiourea and ethylenethiuram monosulphide) are detected during 1.5-2 months. Zineb persists longer on cherries, grapes, and especially on European black currants.

In the USSR, it is prohibited to treat black currants and onions planted for their tops with zineb.

Zineb is a protective fungicide preventing the development and propagation of various diseases. In some cases, the local systemic action of zineb is noted against late blight of potatoes and blue mould of sugar beets. It is effective against grapevine mildew, late blight of potatoes and tomatoes, blue mould of tobacco, scab of apples and pears, cercosporosis of sugar beets and many other diseases of vegetable, fruit, technical and melon crops. Zineb is marketed in the form of an 80% wettable powder and is used during the vegetation period by spraying plants with a 0.7% suspension at a rate of 4-8 kg/ha for treating grapevines and orchards, 3-6 for berry patches, 2-4 for field and melon crops, 8 for hops, and 4 kg/ha for tobacco. Zineb is used by aerial spraying of 5% suspensions at a rate of 5 kg/ha to control wheat rust. Treatment is begun before the disease appears (according to a forecast) or when the pustules of the first generation appear. The following treatments are performed in 7-10 days.

Zineb does not inhibit powdery mildews, and when used perenially for two or three years on the same grapevines, it leads to disturbing of the growth and development of the vines and intensification of the development of oidium. This is why it is recommended to alternate

treatments with zineb and with copper-containing compounds. Before blossoming terminates, it is good to use zineb, and after it terminates, Bordeaux mixture. The use of zineb together with colloidal sulphur gives good results for the simultaneous inhibition of a variety of diseases.

Zineb is compatible with most pesticides except lime sulphur and Bordeaux mixture.

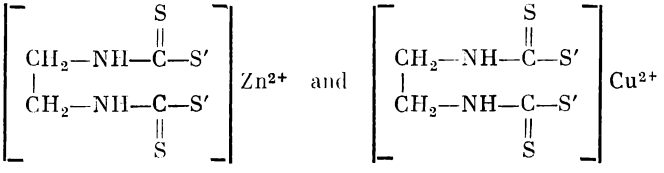
Zineb has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 1850 mg/kg). It has a slight blastomogenic, mutagenic, and embryotoxic action. Its chronic toxicity is slight. It may cause allergic infections of the skin, and asthmatic phenomena. During the first days after the treatment of plants, carbon disulphide, hydrogen sulphide, and other products of zineb decomposition may accumulate in the air in concentrations dangerous to the health. For this reason, workers must use antigas respirators and other means of individual protection on fields treated with zineb.

The maximum tolerated concentration in the air of the working zone is 0.5 mg/m^3. The tolerance level in vegetable food products is 0.6 mg/kg, and in grain is 1 mg/kg.

The harvest time for grapevines is 30 days, for tobacco—8-10 days, and for other crops—20 days.

Cuprozin-1

This is a formulation containing jointly prepared zinc and copper salts of ethylenebisdithiocarbamic acid (in the ratio of 9:1):



It is a brown powder insoluble in water and most organic solvents. It decomposes in water and an acid medium. It is moderately stable in the environment. It is not detected in potato tubers in 20 days after treatment, while in black currant berries it is detected in considerable amounts exceeding the tolerated ones. This is why the treatment of black currants with this formulation is prohibited.

The substance is marketed in the form of a 70% wettable powder.

It is used against mildew and anthracnose of grapevines, late blight of potatoes and tomatoes, and blue mould of sugar beets. The concentration of the working solutions for spraying is 0.4% of the formulation, and the rate of use is 2.4-6 kg/ha. The harvest time is 20 days.

Cuprozin-1 is only slightly toxic to humans and warm-blooded animals (LD_{50} for rats with one ingestion is 4080 (mg/kg).

It has moderate cumulative action. The maximum tolerated concentration in the air is 0.5 mg/m³, and the tolerance level in vegetables and fruits is 1 mg/kg.

Polymarzin

Polymarzin is a combined formulation containing the zinc and manganese salts of ethylenebisdithiocarbamic acid and ethylenethiuram sulphide:

$$[-CH_2-NH-C(S)-S-Zn-S-C(S)-NH-CH_2-]_n$$
$$[-CH_2-NH-C(S)-S-Mn-S-C(S)-NH-CH_2-]_m$$
$$[-CH_2-NH-C(S)-S-S-C(S)-NH-CH_2-]_k$$
$$n:m:k=1:2:2$$

The formulation is a yellow odourless powder insoluble in water and slightly soluble in acetone and benzene. It is soluble in alkalies, chloroform, and trilon B. It is unstable in acid and alkaline media, which is why it may not be used together with lime, lime sulphur, or Bordeaux mixture.

It is marketed in the form of a 70% wettable powder. It is highly effective in controlling the pathogens of late blight of potatoes and tomatoes. It is used for treatments during vegetation in a concentration of the formulation of 0.4% at a rate of 2.4-3.2 kg/ha. The harvest time is 20 days.

It is compatible with most pesticides.

Polymarzin is only slightly toxic to humans and warm-blooded animals (LD_{50} for rats is 3290 mg/kg). Its cumulative properties are low, it may have an embryotoxic effect and has slight allergenic properties. The maximum tolerated concentration in the air of the working zone is 0.5 mg/m³. The tolerance level in tomatoes and potatoes is 0.1 mg/kg.

Metiram (Polycarbazin, Polyram, Polyram-Combi)

This is a combined formulation containing zinc ethylenebisdithiocarbamate and ethylenebisthiuram polysulphide:

$$[-CH_2-NH-C(S)-S-S-C(S)-NH-CH_2-]_n$$
$$[-CH_2-NH-C(S)-S-Zn-S-C(S)-NH-CH_2-]_m$$
$$n:m=1:3$$

It is a light yellow solid insoluble in water and organic solvents. It dissolves well in weak aqueous solutions of alkalies.

It is unstable in strong acid and alkaline media, and decomposes under the action of mineral acids. It is moderately stable in the environment. It persists in water over 30 days. The hydrolysis products are ethylenethiuram monosulphide, ethylenethiourea, and sulphur. Its half-life on the fruits and leaves of apple trees is 8 and 25 days, respectively.

Metiram is a contact fungicide with protective action. It is marketed in the form of a 75% wettable powder. It is intended to control apple and pear scab, grape mildew, late blight of potatoes and tomatoes, blue mould of tobacco, blue mould and cercosporosis of sugar beets, and wheat rust at a rate of 2-8 kg/ha. It is compatible with many pesticides.

Several treatments with a 0.4% working solution are performed to monitor apple scab: the first one in the period when the flower buds separate and become pink, the second immediately after blossoming, and the following ones at intervals of 10-12 days. The harvest time is 20 days.

Metiram in a concentration of 0.4% is also used to control late blight of potatoes, with the first treatment in the period of flower bud formation—the beginning of blossoming, and the following ones (as required) in 10-15 days.

Sugar beets are treated against cercosporosis and blue mould when the first indications of the disease appear, and then every 10-15 days. The harvest time is 20 days.

Metiram is compatible with most formulations. It must not be used in combination with acid or strongly alkaline substances.

Metiram has a low toxicity to humans and warm-blooded animals (LD_{50} for rats upon ingestion is 6100 mg/kg). The cumulative effect is slight. Embryotoxic and teratogenic effects appear upon the repeated action of large amounts of metiram.

It is slightly dangerous to bees. They should be isolated for one day during treatments.

The tolerance level in food products of a vegetable origin is 1 mg/kg. The maximum tolerated concentration in the air of the working zone is 0.1 mg/m^3.

Mancozeb (Manzeb, Dithane M-45)

The active ingredient is a complex of zinc ions (2%), manganese (16%), and ethylenebisdithiocarbamate (62%). It is a grayish-yellow powder dissolving slightly in water and most organic solvents. It is stable in ordinary storage conditions, but decomposes before melting when heated. This contact fungicide with protective action can be used as a highly effective substitute for Bordeaux mixture. It is marketed in the form of an 80% wettable powder.

Mancozeb is recommended for pilot use to protect potatoes and tomatoes against late blight and grapevines against mildew. The harvest time is 20 days.

Plants are sprayed during their vegetation period with a 0.2% suspension at a rate of use of the formulation of 1.2-3 kg/ha.

Mancozeb has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is over 6000 mg/kg).

7.6. Combined Use of Copper Compounds and Dithiocarbamic Acid Derivatives

Upon the prolonged regular use of the same fungicides, the pathogens become adapted to them and their resistance to the fungicide used grows. For instance, an increase in the resistance of phytophthora to copper formulations was noted.

The repeated application of Bordeaux mixture and copper oxychloride has a negative effect on the plants being protected, causing depression of photosynthesis, dehydration of the leaves, inhibition of the growth of shoots, and damage to fruits, especially if the plants were treated after the fruits formed. To diminish the negative effect of copper-containing formulations on plants, treatments with them are alternated with the use of derivatives of dithiocarbamic acid, which are not phytotoxic and, as a rule, facilitate the sanitation of the plants.

Upon the prolonged use of zineb against grapevine mildew, however, in the second and third years improper growth and more intense infection with oidium were noted.

Although the spectrum of fungicidal action of these groups of substances is close, for individual pathogens their toxicity and nature of action are different. For example, dithiocarbamic acid derivatives are the most effective against blue mould of tobacco, whereas the pathogen of this disease exhibits an increased resistance to copper-containing substances.

With respect to grape mildew, copper formulations exhibited a higher genostatic activity (prevented spore-bearing) than zineb and metiram.

To improve the effectiveness of fungicides of these groups, there were tested mixtures of zineb with copper oxychloride (cuprosan and miltox special), and of metiram with copper oxychloride (polychom). The mixtures of these substances were not inferior in their effectiveness to their constituent parts when used individually, while in a number of cases they were more effective, especially if the copper-containing substances predominated in a mixture. The advantages of the mixtures used to control grape mildew displayed themselves especially clearly in epithytotic years. The mixtures inhibited mildew, and limited the development of oidium and gray rot.

Cuprosan

The active ingredient, a mixture of zineb and copper oxychloride, is a bluish-green odourless powder.

It is marketed in the form of an 80% wettable powder containing 65% copper oxychloride and 15% zineb.

Cuprosan persists better on the surface of treated plants than zineb, is superior in its effectiveness to Bordeaux mixture, and does not produce burns.

It is used for treating apples, pears, plums, peaches, apricots, currants, gooseberries, raspberries, grapevines, sugar beets, potatoes, tomatoes, watermelons, canteloupes, cucumbers, and hops against the same diseases for whose control copper oxychloride and zineb are effective.

For the low-volume aerial spraying of grapevines, cuprosan is used at a rate of 5 kg/ha with the addition of the antivaporizer AI-4P.

The plants are sprayed during their vegetation period with 0.4% suspensions. The harvest time is 20 days.

Cuprosan is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 400 mg/kg). Its cumulative properties are pronounced, and the cumulation coefficient is 0.9.

The maximum tolerated concentration in the air of the working zone is 0.1 mg/m^3, and in water basins, 0.1 mg/litre.

The tolerance level in vegetables, fruits, grapes, and melons is 0.1 mg/kg (with respect to the copper oxychloride).

Miltox Special

This formulation is a mixture of zineb and copper oxychloride. It is marketed in the form of a 57% wettable powder containing 37% of copper oxychloride and 20% of zineb.

It is recommended for treating grapevines during their vegetation period using 0.4% suspensions at a rate of 4-6 kg/ha.

Polychom

Polychom is a mixture of metiram with copper oxychloride. It is marketed in the form of an 80% wettable powder containing three parts of 75% metiram and one part of 90% copper oxychloride.

It is recommended for the treatment of apples, pears, grapevines, sugar beets, potatoes, tomatoes, and hops during their vegetation period for controlling the same diseases against which copper oxychloride and metiram are effective.

Treatment is conducted using 0.4% suspensions at a rate of 2.4-8 kg/ha. The harvest time is 20 days.

7.7. Compounds Containing Phthalimide Groups

Substances of this group are distinguished by their high fungicidal action.

In the USSR, it is permitted to use captan—a derivative of tetrahydrophthalic acid, and folpet—a derivative of phthalic acid. Captan and folpet are effective against downy mildew fungi, and have a specific activity against fruit spot. Folpet also inhibits the development of powdery mildew fungi.

The main decomposition products of captan and folpet on plants (phthalimide and tetrahydrophthalimide) have a noticeable teratogenic action.

These substances decompose comparatively rapidly in the soil under the influence of microorganisms with the formation of the relevant imides, which as a result of hydrolysis transform into the corresponding acids with the subsequent complete decomposition of a molecule. This process lasts several months.

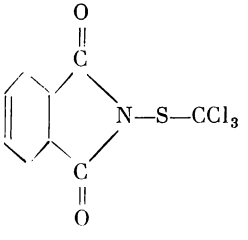
The fungicides can be detected on the surface of plants for a comparatively long time (up to two months), penetrating into the tissues only in insignificant amounts.

The washing of vegetable products with water substantially lowers the residual amounts of captan and folpet. Captan is very toxic to fish and inhibits the development of many soil microorganisms.

Captan and folpet have a low toxicity to humans and warm-blooded animals, but react with the sulphhydril groups of proteins. This is why workers using these fungicides are recommended to choose food rich in proteins.

Captan (Orthocide)

The active ingredient is N-{(trichloromethyl)thio}-4-cyclohexene-1,2-dicarboximide (or N-trichloromethyl-thio-tetrahydrophthalimide):



It is a white crystalline substance with a slight odour melting at 175 °C. It is virtually insoluble in water (less than 0.5 mg/litre at room temperature) and well soluble in acetone, benzene, chloroform, carbon tetrachloride, and dichloroethane.

Captan is prepared by reacting tetrahydrophthalimide with perchloromethylmercaptan.

The technical product is a yellow or gray substance with the specific odour of perchloromercaptan and thiophosgene melting at 164 °C.

Captan is stable, but rapidly hydrolyzes when moist. This process is accelerated in the presence of alkalies and at an elevated temperature. As a result of hydrolysis, tetrahydrophthalimide is formed, and hydrogen chloride, carbon dioxide, and sulphur are evolved.

The large amount of hydrogen chloride liberated in hydrolysis results in the decomposition of various materials, therefore captan must never be packed in paper containers.

It must be stored in dry premises.

Captan is incompatible with all pesticides having alkaline properties. It must not be mixed with Bordeaux mixture, lime sulphur, or lime.

Captan is a contact fungicide with protective action. It is characterized by a fungicidal and slight bactericidal action. It is marketed in the form of a 50% wettable powder (45% of kaolin, 2% of OP-7, and 3% of sulphide-alcohol slops). It is mainly used for treating vegetating plants.

Captan is used as a substitute for Bordeaux mixture in concentrations of 0.5% at a rate of 2.5-10 kg/ha. It has a broad spectrum of action, but the duration of its protective action is less than that of Bordeaux mixture and is 7-14 days.

Captan is especially effective against spots and blights, particularly against the blossom blight of peaches. It is used against mildew, rots of grapes, late blight and alternaria leaf spot of potatoes and tomatoes, clusterosporiosis of stone fruits, gray rot and spot of strawberries, anthracnose of berry patches, and scab of apples and pears. The first treatment of apples is performed before blossoming in the pink flower bud phase, the second—during blossoming, the third—at the end of blossoming, and the following ones every one or two weeks. The harvest time for apples and pears is 30 days, for grapes—60, and for tomatoes, potatoes, and melons—20 days. Captan persists for a comparatively long time on the surface of treated plants, and is detected in one or two months and even more. To reduce the captan content in vegetable products, they are washed with water and a 2% solution of calcium hydroxide.

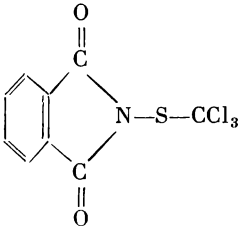
Captan does not burn plants and improves the keeping qualities of fruits in storage. It is compatible with many pesticides except for mineral oils, alkaline substances, DNOC, and green vitriol.

The regular use of captan against apple scab is attended by a growth of powdery mildew in the relevant areas. Consequently, it must be alternated with other fungicides.

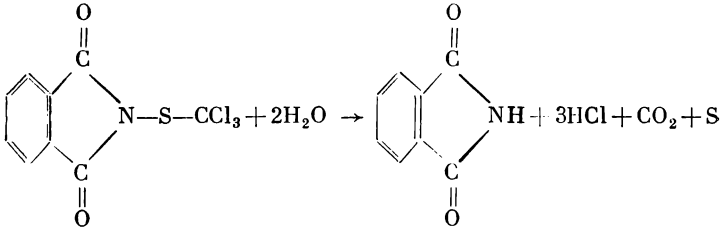
Captan has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 9000-12 500 mg/kg); when animals are kept on a low-protein diet, LD_{50} is 480 mg/kg. Its chronic toxicity is low. Embryotoxic and mutagenic action has been revealed. The tolerance level in food products is 0.3 mg/kg.

Folpet (Phaltan)

The active ingredient is N-(trichloromethylthio) phthalimide:



It is a crystalline substance melting at 177 °C. It is insoluble in water (1 mg/litre at room temperature), is stable in the dry state, but readily hydrolyzes, especially in an alkaline medium:



In connection with the rapid hydrolysis of folpet, its persistence on the surface of treated plants is less than that of captan, and the period of protective action is 5 or 6 days.

It is marketed in the form of a 50% wettable powder. It must be stored in dry conditions, and not in paper containers.

Folpet is a contact fungicide having a protective and a slight curative action. It causes plasmolysis, and then partial or complete breaking up of a mycelium. It has an inhibiting effect on powdery mildew, which is probably associated with the evolution of elementary sulphur in hydrolysis.

Folpet is used as a substitute for Bordeaux mixture in concentrations of 0.5% at a rate of 3-10 kg/ha. The harvest time is 20 days. In plant protection practice, folpet is used to treat apple, pear, plum, peach, apricot, and cherry trees, gooseberries, currants, potatoes, and tomatoes. It is especially effective against a group of diseases of grapevines—mildew, anthracnose, red, black, white, and

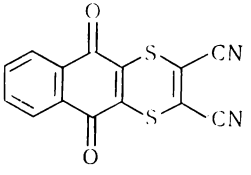
gray rot. It inhibits the development of oidium. It is compatible with most pesticides except for alkaline ones, and also for mineral oils and formulations based on them.

Folpet has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is about 10 000 mg/kg). It has a slight cumulative toxicity, is embryotoxic, and may irritate mucous membranes. Workers using it must reliably protect their eyes and respiratory organs.

The tolerance level of folpet in vegetable food products is 2 mg/kg. The maximum tolerated concentration in the air of the working zone is 2 mg/m^3.

Dithianon (Delan, Thynon)

The active ingredient is 5,10-dihydro-5,10-dioxonaphtho-(2,3b)-*p*-dithiin-2.3-dicarbonitrile:



It forms brown odourless crystals melting at 230 °C, insoluble in water (about 0.05 mg/litre at room temperature), and soluble in dioxane and chloroform. Dithianon is stable in an alkaline medium. It is a fungicide with prolonged action exhibiting a high effectiveness and recommended for use against apple and pear scab and grape mildew.

Dithianon is marketed in the form of a 75% wettable powder used in a concentration of 0.2% at a rate of 2-4 kg/ha. The harvest time is 20 days.

Dithianon is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 514 ± 95 mg/kg) and has a low toxicity to bees.

7.8. Sulphur and Its Compounds

Practical use has been found by formulations of elementary sulphur (ground, colloidal sulphur, and a wettable sulphur powder) and lime sulphur.

Sulphur formulations are highly effective fungicides against powdery mildew fungi and various spot and blights; they inhibit the development of scab to a lower extent, and have acaricidal properties. They have a protective and curative action against diseases. Spores treated with sulphur lose their ability of sprouting.

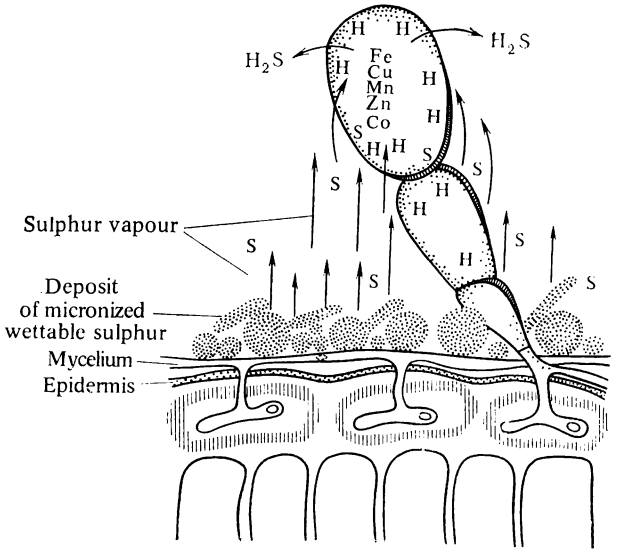


Fig. 14. Mechanism of action of sulphur fungicide (micronized wettable sulphur) on powdery mildew (after A. Wilhelm)

The fungicidal activity of sulphur formulations is explained by their ability to liberate a vapour of elementary sulphur that penetrates into the spores or mycelia of a fungus owing to dissolving in the substances of the cell, most probably in the lipids (Fig. 14). Sulphur, being an acceptor of hydrogen, disrupts the normal course of hydrogenation and dehydrogenation reactions, with the formation of hydrogen sulphide. The latter is closely associated with the growth of spores and the vitality of the fungus. Spores that have lost their ability of growing cannot form hydrogen sulphide from sulphur. Consequently, the formation of hydrogen sulphide can be considered as detoxification of the elementary sulphur. But hydrogen sulphide is fungitoxic and inactivates vitally important enzymes—catalase, cytochromoxidase, and lactase. Elementary sulphur can also bind the metals (iron, copper, manganese, zinc) contained in the enzymes and form sulphides. All this upsets the normal metabolism of fungi and causes them to perish.

It is presumed that the specific nature of the action of sulphur formulations is explained by the different ability of spores to absorb the sulphur and detoxify it with the formation of hydrogen sulphide.

In view of the above notions on the nature of the fungitoxic action of sulphur formulations for the successful control of diseases, it is essential that the formulations used gradually (during a long time) evolve an amount of sulphur vapour sufficient for a fungicidal action

as close as possible to the mycelium and conidia of a fungus. This is ensured by the uniform coating by the fungicide of the surface being protected, and by the use of formulations having a good retainability and persistence.

Ground sulphur formulations consisting of coarse particles are retained poorly on the surface of plants, and have a smaller and non-uniform evaporation surface.

Colloidal sulphur formulations have the largest surface area and intensity of evaporation owing to their consisting of very minute particles, but the duration of their action is brief. Formulations of highly dispersed sulphur consisting of particles from 1 to 20 μm in size have the best fungicidal action. They are retained well and are uniformly distributed over a plant, and have a sufficiently large evaporation surface and duration of action.

The fungicidal action of lime sulphur is also associated with the evolution of elementary sulphur.

The action of sulphur formulations is greatly affected by the ambient temperature. At a temperature below 20 °C, they are only slightly effective, while above 35 °C they harm plants. Many varieties of gooseberries and cucurbit crops are distinguished by their high sensitivity to sulphur formulations: when treated with sulphur formulations, burns may occur, as well as roughening and frangibility of the leaves, and sometimes even defoliation. Sulphur formulations must never be used on crops suffering from drought (if necessary, the crops must be watered before treatment). Sulphur formulations may not be mixed with oils, therefore treatment with sulphur may be performed 15 days before or after spraying with oils.

Sulphur formulations are generally used from the moment of the appearance of a disease. The treatments are repeated as needed every 7-10 days. The proper application of sulphur formulations facilitates an increase in the yield of crops and an improvement in their quality.

Sulphur formulations have a low toxicity to humans and warm-blooded animals. The prolonged inhalation of sulphur dust may lead to an ailment of the lungs, therefore when working with formulations of elementary sulphur, one must use antidust respirators. Formulations of elementary sulphur may be used without any restrictions. The harvest time for all crops except medicinal ones is one day. Cucumbers in greenhouses must be washed before harvesting them. No tolerance levels have been established for the sulphur content in food products.

Ground Sulphur

This is a pale yellow powder consisting of angular particles from 4 to 250 μm in size. It contains 95-99% of elementary sulphur. Its density is 2.07, and it melts at 112.8 °C. It does not dissolve in wa-

ter and is wetted poorly by it. It dissolves in carbon disulphide and carbon tetrachloride. It evaporates slowly in the air.

The formulation is not hygroscopic and does not cake in storage, but the particles are easily electrified and stick together to form small loose lumps. Ground sulphur is capable of self-ignition, therefore it must be kept away from mineral fertilizers, especially nitrogen ones. It is applied by dusting at a rate of 15-30 kg/ha. It is desirable to dust plants over dew in fine weather at a temperature above 20 °C, but not in the hottest part of the day (to prevent burns).

Ground sulphur is effective as a protective and curative fungicide against powdery mildew of various crops, rust diseases, and also against phytophagous mites. When properly used, it does not damage plants, except (as indicated above), certain varieties of gooseberries and melon crops.

Colloidal Sulphur and a Wettable Powder

Colloidal sulphur is prepared by chemical means when purifying gases of hydrogen sulphide. It is marketed in the form of a paste containing 70% of elementary sulphur. The formulation must be packed in a moistureproof container, otherwise it dries and forms lumps, the suspension prepared from such a formulation is of a poor quality.

A wettable powder of sulphur is prepared by grinding coarsely dispersed sulphur in special mills (micronizers). Sulphur is insoluble in water, therefore, to make its particles wettable, stabilizers and wetting agents are added to the sulphur formulations. A wettable sulphur powder is of a yellow-gray colour and contains 90-95% of elementary sulphur.

The wettable powder and the colloidal sulphur paste are used to treat many crops (Table 15) by spraying in concentrations of 0.2-1% at rates of 2-16 kg/ha. The high stability of the working solutions and the good wetting by them of the surface being treated ensure a higher effectiveness of wettable and colloidal sulphur than of the ground formulation.

Wettable and colloidal sulphur are used to control powdery mildew of cucumbers (0.3-0.5% concentration), gooseberries (0.3-0.6% concentration), beets, the oidium of grapes, powdery mildew and scab of apples (0.5-1.0% concentration). A 1% suspension of sulphur is used against phytophagous mites.

Apple trees greatly infected with powdery mildew are sprayed in the period of bud opening with a 1% suspension of wettable sulphur.

The subsequent treatments are performed with lowering concentrations from 0.7 to 0.2% before blossoming and after blos-

Table 15. Use of Colloidal Sulphur (Paste and Wettable Powder)

Crop	Disease	Time of first treatment
Apples and pears	Powdery mildew, rust	Before blossoming (when flower buds separate and become pink)
Beans and peas	Powdery mildew	When disease appears
Carrots, celery, parsley, parsnip	Ditto	Ditto
Cotton	Ditto	Ditto
Cucumbers	Ditto	Ditto
Gooseberries and currants	Anthracnose	After blossoming
	Powdery mildew	Before blossoming
Grain	Powdery mildew	On winter crops at the beginning of plant growth, on spring crops in the stage of 2 or 3 leaves
	Rust	Before the disease appears (according to forecast) or when first generation pustules appear
Grapes	Oidium	At first symptoms of disease Before blossoming
Hops	Powdery mildew	When disease appears
Leguminous perennial grasses	Ditto	Ditto
Raspberries	Rust	Ditto
Stone fruits	Powdery mildew	At first symptoms of disease
Strawberries	Ditto	Before blossoming
Sugar beets	Ditto	When disease appears
Tobacco	Ditto	Ditto
Watermelons and canteloupes	Anthracnose	Before blossoming

soming at intervals of 7-10 days and are continued as long as there is a danger of infection.

In controlling grape oidium (when performing seven treatments), colloidal sulphur reduces the development of the disease from 98 to 22%, and ground sulphur up to 51%.

Treatment with sulphur is discontinued one day before harvesting the crop.

Lime Sulphur

Lime sulphur is prepared at the place of use by boiling sulphur and lime in water for one or two hours. The ratio of water, sulphur, and lime is 17 : 2 : 1. The formed cherry red liquid is settled and filtered to obtain a mother liquor that is used for making the working solutions.

The content of the active ingredient (calcium polysulphides) in the mother liquor depends on the amount of the components and the boiling process (inadequate or too long boiling) and ranges from 10 to 30%.

In practical work, the quality of lime sulphur is determined according to the density (by means of areometers) and is expressed in degrees Baumé by means of special tables. Lime sulphur with a density of 1.285 (32 deg Baumé) is considered to be the best. Actually, however, owing to the low quality of the lime and deviations from the proper boiling technology, the density of lime sulphur prepared at farms does not exceed 1.099-1.116 (13-15 deg Baumé). The mother liquors are kept in glass containers under a layer of kerosene to prevent the access of air. Upon prolonged storage, especially of dilute solutions, the action of the air causes the calcium polysulphides in lime sulphur to decompose with the formation of calcium thiosulphate and thiosulphite, elementary sulphur, and calcium carbonate. This detracts from the fungicidal properties of the lime sulphur, and leads to the formation of a precipitate and of a crust on the surface of the solution. For prolonged storage, dry formulations of calcium polysulphides are prepared by evaporation or drying of the lime sulphur in spray driers. To treat dormant plants, lime sulphur is used in a concentration of 5 deg Baumé (density 1.037 g/cm^3), and in the period of vegetation, in a concentration of 0.5-1-deg Baumé (density 1.007 g/cm^3). The working solutions are prepared from the mother liquor by dilution directly before use. When stored, the working solutions lose their quality, become turbid, acquire a yellow colour, and liberate hydrogen sulphide.

The action of lime sulphur is based on the circumstance that the polysulphides decompose on the surface of plants under the influence of the carbon dioxide and oxygen of the air and evolve finely dispersed sulphur having a fungicidal and acaricidal effect:

$$CaS_x + H_2O + CO_2 \rightarrow CaCO_3 + H_2S + S_{x-1}$$

$$2CaS_x + 3O_2 \rightarrow 2CaS_2O_3 + 2S_{x-2}$$

The thiosulphate formed when oxidized also evolves elementary sulphur:

$$CaS_2O_3 \xrightarrow{O_2} CaSO_3 + S$$

$$CaSO_3 \xrightarrow{O_2} CaSO_4$$

The hydrogen sulphide evolved in the decomposition of the polysulphides also has a fungicidal action. Lime sulphur is effective against scab, powdery mildew of apples and pears, against brown rot, apple-tree cancer, oidium and cercosporosis of grapes, anthracnose of cucumbers and raspberries, powdery mildew of peas, beans, and sugar beets.

Repeated treatments at intervals of 7-8 days are the most effective.

To control currant bud mites, treatment with lime sulphur having a strength of 1.5 deg Baumé is performed before blossoming and a strength of 0.75 deg after blossoming of the currants.

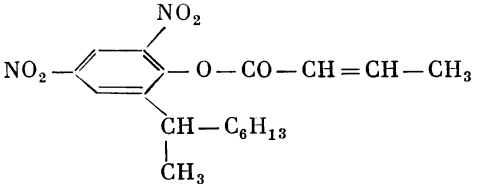
When improperly prepared, stored, and used in increased concentrations, lime sulphur burns plants. To avoid this, the plants should be watered before treatment. Lime sulphur has a low toxicity to humans and warm-blooded animals.

The hydrogen sulphide evolved upon the decomposition of the calcium sulphides is poisonous to humans it, causes burning and pains in the eyes, while when lime sulphur gets onto the skin, it may cause ulcers. One must carefully protect the eyes and skin, and when preparing working solutions—the respiratory organs with an antigas respirator.

7.9. Nitroderivatives of Phenol

Dinocap (Karathane, Crotothane)

The active ingredient is 2,4-dinitro-6-octyl-phenyl crotonate:



It is a viscous liquid boiling at 138-140 °C at 0.05 mmHg. It is virtually insoluble in water and dissolves well in organic solvents. Dinocap is a contact fungicide with protective and curative action effective in controlling powdery mildew fungi. It prevents the growth of the spores of powdery mildew fungi and destroys the mycelium, causing its plasmolysis, and then partial or complete decomposition. In a number of cases, dinocap is more effective than elementary sulphur formulations.

Dinocap protects plants from infection by scab and has an acaricidal effect, but weaker than that of sulphur.

The duration of the protective action of dinocap is 10-14 days. With an increase in the concentration, the protective period grows, but in this case the substance may damage (burn) the plants. In the usually recommended concentrations, dinocap is less phytotoxic than elementary sulphur formulations. Dinocap must never be used with alkaline pesticides or with substances containing oil.

Dinocap is marketed in the form of a 25% yellow wettable powder. It is recommended for controlling powdery mildews of apples and

pears, gooseberries, currants, strawberries, watermelons, canteloupes, and cucumbers. Dinocap is also used for spraying roses and chrysanthema during their vegetation period. It is used in a 0.1% concentration at a rate of 1-3 kg/ha.

The harvest time for fruits and berries is 20 days.

Cucumbers in greenhouses may be treated two days before harvesting them, but the vegetables must be thoroughly washed with water.

Strawberries are treated with dinocap only before blossoming or after harvesting the crop.

Dinocap is highly toxic to humans and warm-blooded animals (LD_{50} for mice is 112.5, and for rats, 600-825 mg/kg), but its cumulative properties are slight. The tolerance level of dinocap in pip fruits and cucumbers is 0.1, and in melons is 1 mg/kg. Its toxicity to bees is low, but they should be isolated for one day during treatments.

Dinobuton (Acrex, Dinofen)

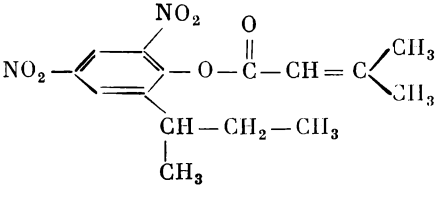
For the physicochemical properties, toxicological characteristic, and the features of use of dinobuton as an acaricide, see p. 161.

Dinobuton is also a fungicide against powdery mildew with a protective and eradicating action. It is recommended for protecting apples, pears, roses, chrysanthema, and pinks with a harvest time of 20 days, currants, gooseberries, and raspberries with a harvest time of 30 days. Cucumbers in greenhouses may be treated with dinobuton during their vegetation period, discontinuing the treatments two days before harvesting the crop provided that the vegetables are thoroughly washed with water. A 50% wettable powder of dinobuton is employed. Spraying is performed with a 0.1-0.15% suspension at a rate of 1.5-3 kg/ha, in greenhouses 6-8 kg/ha. In sheltered soil, dinobuton may cause burning of plants, and it is therefore used in lower concentrations.

Dinobuton is incompatible with alkaline formulations and loses its activity when used with carbaryl.

Binapacryl (Morocide, Acricid, Endosan)

The active ingredient is 2-sec-butyl-4,6-dinitrophenyl-3-methyl-2-butenoate (or 2-sec-butyl-4,6-dinitrophenyl-3-3-dimethylacrylate):



It is a white crystalline powder with a faint aromatic odour melting at 69 °C. It is insoluble in water, is hydrolyzed by concentrated acids and by alkaline solutions, and is decomposed under the influence of ultraviolet radiation. Its solubility in acetone is 78%, in xylene—70%, and in ethanol—11.4%. It is stable in ordinary storage conditions. Its residues persist on plants only briefly. Its fungicidal properties are similar to those of dinocap.

Binapacryl is a fungicide and acaricide. It is marketed in the form of a 50% wettable powder. It is effective against powdery mildew of apples and pears. It is used for spraying seedlings at schools and fruit crop nurseries during the vegetation period in a concentration of 0.2%.

The rate of use is 2-4 kg/ha, with intervals of 10-12 days between treatments.

Binapacryl is effective against spider, citrus red, and hawthorn mites, and also against populations of mites resistant to organophosphorus and organochlorine compounds. It kills all mobile and dormant stages of mites. Its ovicidal action exhibits itself as a result of inhibition of embryonic development because of coagulation of the cytoplasm.

The duration of the acaricidal activity of binapacryl is 15 days. It is compatible with many pesticides except for alkaline and organophosphorus compounds.

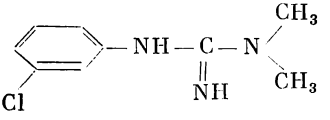
Binapacryl is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 120-165, and for rabbits, 640 mg/kg).

It is characterized by acute chronic and acute dermal toxicity. The tolerance level of binapacryl in fruits, including citrus ones, is 0.002 mg/kg.

7.10. Fungicides of Miscellaneous Groups

FDN

The active ingredient is N,N-dimethyl-N′-3-chlorophenyl-guanidine:



It forms white or light yellow odourless crystals well soluble in acetone, alcohol, ether, benzene, chloroform, and poorly soluble in water and petroleum ether.

It is marketed in the form of a 50% wettable powder containing 50% of the active ingredient, 2% of OP-7, 3% of sulphite-alcohol slops, and 45% of tripoli. It is stable in storage.

FDN is a contact highly selective fungicide with protective and curative action. It is effective against powdery mildew of cucumbers, having an eradicating contact action when the plants are sprayed, and a systemic action when it is incorporated into the soil.

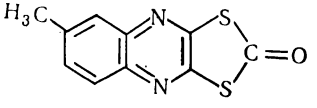
It persists up to 18-20 days, and has a high activity at various temperatures. For example, lowering of the temperature from 27 to 18 C did not change the activity of FDN.

Spraying is performed with a 0.2% suspension during the vegetation period at a rate of 2-4 kg/ha. The harvest time is 20 days.

The substance is moderately toxic to humans and warm-blooded animals (LD_{50} for rats upon oral ingestion is 160-233 mg/kg).

Quinomethionate (Chinomethionat, Oxythioquinox, Morestan)

The active ingredient is 6-methyl-1,3-dithiolo(4,5-b) quinoxalin-2-one:



It forms yellow odourless crystals melting at 172 °C and insoluble in water. It decomposes in an alkaline medium. It is slightly soluble in organic solvents such as acetone and alcohol, and soluble in hot benzene, toluene, dioxane, and dimethyl formamide.

It is a contact substance with protective and eradicating action. The duration of its action is at least 15 days, and even longer in the absence of precipitation.

Quinomethionate is effective in controlling powdery mildew, and also has acaricidal properties.

It is marketed in the form of a 25% wettable powder.

The optimal concentrations of the formulation for spraying are 0.03-0.05%, and the rates of use are 0.5-1 kg/ha.

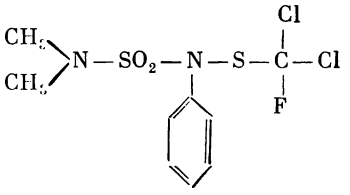
Quinomethionate is recommended only for spraying seedlings and cuttings in nurseries of apple and pear trees and grapevines during the vegetation period.

Its use is limited in connection with its sharply pronounced cumulative properties.

Quinomethionate has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 2500-3000 mg/kg).

Dichlofluanid (Euparen, Elvaron)

The active ingredient is N′-dichlorofluoromethylthio-N,N-dimethyl-N′-phenylsulphamide:



It is a white powder melting at 105.0-105.6 °C, insoluble in water and soluble in acetone, methanol, and xylene. It decomposes in alkaline media and in the presence of polysulphides.

In natural conditions on plants in the presence of moisture, it hydrolyzes to form N,N-dimethyl-N′-phenyldiamide sulphate.

Dichlofluanid is a fungicide with a broad spectrum of action. It is especially effective in controlling gray rot of various crops, inhibits powdery mildews, and has acaricidal properties. Dichlofluanid has proved its effectiveness on grapevines against mildew, oidium, and gray rot.

It gives especially good results against gray rot and leaf spot of strawberries.

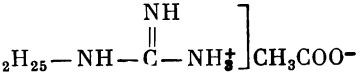
Dichlofluanid is marketed in the form of a 50% wettable powder. It is used in concentrations of 0.2-0.4% at a rate of 2-8 kg/ha. The treatment of grapevines is commenced before blossoming and is stopped 30 days before harvesting the crop. Strawberries are sprayed before blossoming and after harvesting the crop. Apple trees are treated with 0.4% suspensions with a harvest time of 20 days. It is compatible with most pesticides except for alkaline ones and those used in the form of emulsifiable concentrates.

Dichlofluanid has a low toxicity to humans and warm-blooded animals (LD_{50} for mice is 1850 mg/kg). The tolerance level in vegetable food products is 1.3 mg/kg. No residues are tolerated in strawberries. The metabolite of dichlofluanid formed on plants (N,N-dimethyl-N′-phenyldiamide sulphate) is twice as toxic as the initial substance.

The cumulative properties are moderate. It is harmless to bees.

Dodine (Tsitrex, Cyprex, Carpene, Syllit)

The active ingredient is *n*-dodenylguanidine acetate:



It forms white crystals melting at 136 °C, well soluble in hot water and ethanol. It is stable in weak solutions of acids, while a strong alkali causes it to decompose with the evolution of a base.

Dodine is a narrowly specialized fungicide recommended for controlling scab of apple trees; it is also effective against coccomycosis of stone fruits.

The active ingredient of dodine has properties of a surfactant. It is retained very well on a plant, and is distributed and redistributed over it, including the growing shoots. It is a protective contact fungicide, but has an eradicating and local penetrating effect; it penetrates well into leaves and inhibits an infection developing in them.

The protective action of dodine manifests itself at concentrations of 0.03-0.07%, and its curative action at 0.15-0.20%.

It is marketed in the form of a 65% wettable powder.

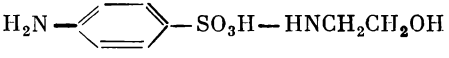
Dodine is used in a concentration of 0.15-0.20 % at a rate of 2-4 kg/ha.

Apple trees are treated with dodine for controlling scab when the first indications of the disease appear at the times recommended for Bordeaux mixture (the first treatment when the flower buds begin to turn pink, and the second immediately after blossoming). Depending on the climatic conditions and the degree of development of the disease, from three to seven treatments are performed during a season at intervals of 10-15 days. The harvest time is 20 days. The use of dodine in increased concentrations may lead to burning of the leaves, and a net may appear on fruits with a thin skin. It is compatible with most formulations except for lime sulphur, dinocap, oils, and oil emulsions.

Dodine is slightly toxic to humans and warm-blooded animals (LD_{50} for rats is 1118 mg/kg), but has a strong irritating effect on the skin and mucous membranes. The tolerance level in fresh fruit is 0.6 mg/kg. The maximum tolerated concentration in the air of the working zone is 0.1 mg/m^3, and in water basins is 0.005 mg/litre.

Anilat

The active ingredient is the monoethanolamine salt of sulphanilic acid:



It dissolves well in water and alcohol, and is insoluble in ether and benzene. It is not volatile, and is comparatively stable in aqueous solutions and various media. When its aqueous solutions are acidified, it decomposes with the formation of sulphanilic acid.

Anilat is a contact fungicide with protective and eradicating action. It is highly effective in controlling stem, brown, and stripe rust

of wheat. It has a curative action, therefore it is effective both before and after the appearance of a disease. Anilat completely removes rust pustules from wheat leaves, chlorotic spots remaining instead of them.

When used to treat seeds, anilat is also effective against barley smut and root rots of wheat. It is recommended for treating seeds in primary seed production in a dose of 1-3 kg/tonne.

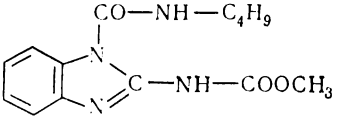
An anilat formulation contains 93% of the active ingredient. It is used for spraying wheat in a 1% concentration at a rate of 5-10 kg/ha. Aerial spraying is performed with 5-10% solutions two or three times during the vegetation period, using the working liquid at a rate of 100 litre/ha. The harvest time is 20 days.

Anilat has a low toxicity to humans (LD_{50} for rats is 5380 mg/kg). Its cumulative properties are slight.

7.11. Systemic Fungicides

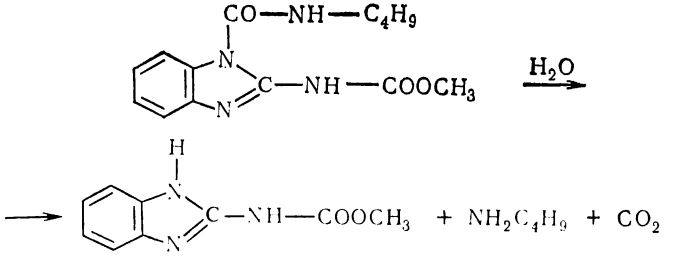
Benomyl ***(Benlate)***

The active ingredient is methyl-1-(butylcarbamoyl)-2-benzimidazolecarbamate:



The pure substance is a white crystalline solid with a faint acrid odour, slightly soluble in water (3.8 mg/litre at pH 7 and 20 °C) and oils; its solubility in chloroform is 94 g/kg. It is not volatile, and when heated decomposes before melting.

In an aqueous medium, benomyl decomposes into methyl benzimidazol-2-yl carbamate (carbendazim), butylamine, and CO_2:



Carbendazim is formed under the action of ultraviolet rays, when heated, and when stored in the presence of moisture, and is the main

metabolite of benomyl in plants. Carbendazim also has a fungicidal action. The metabolites discovered in the soil, in addition to carbendazim, contain 2-aminobenzimidazole. These metabolites are relatively stable and are only slightly leached out beyond the limits of the treated plot.

Benomyl persists for a long time on treated foliage in sheltered soil and in field conditions.

It migrates in a plant only in an acropetal direction, upward along the xylem, and does not migrate along the phloem. Its systemic action exhibits itself when it penetrates through the roots, in the treatment of seeds, application to the stem or into the axils of a leaf. Benomyl is absorbed by leaves, but does not migrate from one leaf to another in fungicidal amounts.

Benomyl is a systemic and contact fungicide with protective and curative action. It displays properties of an acaricide, and owing to its ovicidal action inhibits spider mites and melon aphids. It is slightly toxic to the predatory mite phytoseiulus.

Benomyl is effective in controlling diseases caused by powdery mildews, vascular wilt diseases caused by the species *Verticillium* Nees, *Fusarium* Link, *Rizoctonia* D.C., and rots caused by *Botrytis cinerea*. Benomyl has no effect on bacteria, phycomycetes, species of the genera *Helmintosporium* Link, *Alternaria* Nees, and *Sclerotium Rolfsii* Sace. The fungicidal action of benomyl is due to disruption of the reproductive ability of fungi. It is assumed that the mechanism of action of benzimidazole derivatives is associated with disarrangement of biosynthesis or of the functions of the purine bases.

It is employed in controlling apple scab, powdery mildews of cucumbers, cercosporosis of sugar beets, gray rot and powdery mildew of strawberries, brown rot and powdery mildew of wheat, cotton wilt, oidium and gray rot of grapes, and brown patch of tomatoes.

Benomyl is marketed in the form of a 50% wettable powder. It may be used for the treatment of vegetating plants, incorporation into the soil, and the dressing of seeds. The effectiveness of benomyl when treating plants grows if 0.03% of a surfactant is added to the working solution directly before use. In this case, the formulation is retained better on the treated surface and is washed off less by atmospheric precipitation. To ensure uniform treatment, it is good practice to apply benomyl with an increased rate of use of the working liquid.

To control scab and powdery mildew of apple trees, benomyl is used in a concentration of 0.1% at a rate of 1-2 kg/ha. The first spraying is performed before blossoming when the flower buds turn pink, the second—at the end of blossoming or immediately after it, and the following treatments—every 10-15 days. The harvest time is 20 days. Benomyl has a curative effect against scab during four days after treatment, after which it has a protective systemic effect.

Benomyl is superior to all other fungicides in its effectiveness against cercosporis of sugar beets. To protect the latter, it is used in a 0.1% concentration at a rate of 0.6-0.8 kg/ha. The first spraying is performed when the first symptoms of the disease appear, and the following ones every 10-15 days. Benomyl is used in the same way for controlling powdery mildew of cucumbers.

Benomyl has a protective and curative effect against powdery mildew of cucumbers when incorporated into the soil in an amount of 1.2 g/cm^2, and also a protective systemic effect in the treatment of cucumber seeds at a rate of 4-6 g/kg.

To control cotton wilt, benomyl is incorporated into the soil in the drill rows when sowing, or in the inter-row spacings over the shoots with obligatory placement at a depth of 5-10 cm, or in fall ploughing in an amount of 75-150 kg/ha.

Benomyl is very persistent in the soil; the soil microorganisms decompose it very slightly, and it migrates along the soil's profile to a depth of up to 20 cm.

Benomyl is compatible with most pesticides and fertilizers for spray nutrition.

When properly used, benomyl is not toxic to cultural plants, but when increased amounts of benomyl are incorporated into the soil, the toxic action of the fungicide on plants is observed.

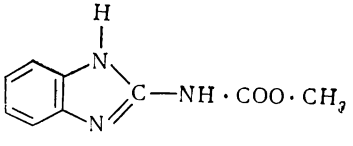
Benomyl is employed for protecting many plants during their vegetation period. The harvest time is 7 days for cucumbers, 10 days for grapes and tomatoes, 15 days for currants, and 20 days for sugar beets, apples, pears, and wheat.

The regular use of benomyl caused the appearance of resistant races of pathogens. Treatment with other fungicides, however, resulted in the disappearance of the acquired resistance.

Benomyl has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 9500 mg/kg), has no chronic toxicity, and does not irritate the skin. It is slightly toxic to bees, birds, and fish.

Carbendazim (MBC, BMC, Bavistin, Derosal)

The active ingredient is methyl benzimidazol-2-yl carbamate:



It is a light gray powder melting at about 307 °C (decomposes). Carbendazim is sparsely soluble in water (5.8 mg/litre at 20 °C and pH 7) and most organic solvents. It is readily soluble in dimethyl

formamide. It is stable in an acid medium, but slowly decomposes in alkaline conditions with the formation of water-soluble salts. It is compatible with most pesticides.

It is marketed in the form of a 50% wettable powder.

Carbendazim is a contact and systemic fungicide. It is similar to benamyl in its fungicidal activity.

It is not phytotoxic when sprayed on plants, incorporated into the soil, and used to dress seeds. Spraying is performed with 0.2% suspensions at a rate of 1.2-4 kg/ha.

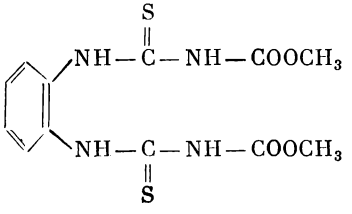
Carbendazim is undergoing state tests to determine its effectiveness in controlling apple tree scab and cucumber powdery mildew, and a set of diseases of grapevines, strawberries, and European black currants.

Strawberries and black currants are treated before blossoming or after harvesting the crop. The harvest time for cucumbers is 10 days, for grapevines is 15 days, and for apples and sugar beets is 20 days.

It has a low toxicity to warm-blooded animals and humans (LD_{50} for rats is 15 000 mg/kg).

Thiophanate-Methyl (Topsil M, NF-44, Cercobin Methyl)

The active ingredient is dimethyl{(1,2-phenylene)bis-(iminocarbonothioyl)}bis{carbamate}, also known as dimethyl 4,4′-*o*-phenylene bis-{3-thioallophanate}:



It is a colourless crystalline solid melting at 168 °C with decomposition. It dissolves slightly in water, sparingly in most organic solvents, and well in acetone, chloroform, and methanol.

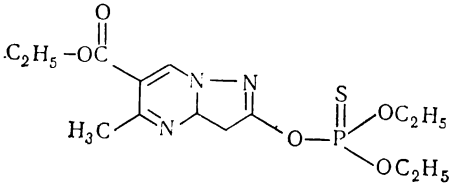
Thiophanate-methyl is a systemic fungicide with a broad spectrum of action. It is similar to benomyl in its fungicidal properties. The main metabolite of thiophanate-methyl, as of benomyl, is carbendazim. The half-life on leaves is 12-15 days. A 70% wettable powder of thiophanate-methyl is marketed. Treatments are performed with 0.1-0.2% suspensions at a rate of 0.6-2 kg of the formulation per hectare. It is compatible with most pesticides except for lime sulphur, Bordeaux mixture, and copper oxychloride.

Thiophanate-methyl has a low toxicity to humans, warm-blooded animals, and bees (LD_{50} for rats is 7450 mg/kg) and slight cumulative properties.

Thiophanate-methyl is recommended for protecting apple, pear, and cherry trees, grapevines, sugar beets, wheat, and barley. The harvest time is 20 days, and for cucumbers, seven days. In sheltered soil, harvested cucumbers must be washed with water.

Pyrazophos (Afugan, Curamil)

The active ingredient is O,O-diethyl-O-(5-methyl-6-ethoxycarbonyl-pyrazolo-{1,5-a}-pyramid-2-yl) phosphorothioate:



It forms colourless crystals melting at 50-51 °C. Its solubility in water is 0.33% at 20 °C. It dissolves well in most organic solvents such as ethanol, toluene, benzene and xylene. It hydrolyzes in the presence of alkalies or acids.

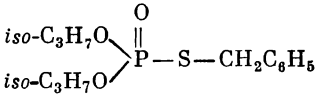
It is marketed in the form of a 30% emulsifiable concentrate containing 32.8% of the technical product, 9.84% of an emulsifier, and 55.66% of organic solvents.

It is stable in storage in a cool and dry spot during one or two years.

Pyrazophos is a systemic fungicide for controlling powdery mildew of various crops. It penetrates well into plants through their leaves and stems and is translocated mainly acropetally. It is recommended for treating cucumbers and other cucurbit crops by spraying the plants during the vegetation period with 0.1% emulsions at a rate of 0.7-1.4 kg/ha. Treatments are commenced when the first symptoms of disease are discovered and are discontinued 20 days before harvesting. It is highly toxic to warm-blooded animals (LD_{50} for rats when introduced orally is 370 mg/kg).

IBP (Ritsid-P, Kitazin-P)

The active ingredient is O,O-diisopropyl-S-benzyl phosphorothioate:



It is a light yellow liquid boiling at 120 °C, slightly soluble in water (1 g/litre at 18 °C) and well soluble in most organic solvents,

including acetone and methanol. It decomposes at a high temperature in an alkaline medium. It also decomposes quite rapidly in water and plants.

IBP is a systemic and contact fungicide with protective and eradicating action. It penetrates well through the underground organs and the root system. It is recommended to control rice pyriculiariosis. The duration of the fungicidal action is 5-10 days.

A 50% emulsifiable concentrate is marketed. It is used for the aerial spraying of rice during the vegetation period at a rate of the formulation of 1-2 kg/ha, and of the working liquid of 200 litre/ha.

The first treatment is performed prior to the heading of panicles, the second, after blossoming, and the following treatments, every 10 days. The harvest time is 20 days.

IBP belongs to moderately toxic fungicides (LD_{50} for mice when introduced orally is 660 mg/kg).

7.12. Fungicides Used for Treating Seeds and Planting Stock

The disinfection of seeds and planting stock by chemical substances is aimed at protecting the plants against pathogens that are on the surface of seeds (common bunt of wheat, covered smut of barley, flag smut of rye, loose smut of millet, etc.), in and under the hull of seeds (loose smut of oats, leaf blight of wheat, polysporiosis of flax, white rot of sunflowers), and also inside seeds in the embryon (loose smut of wheat and barley).

Seed protectants, as their name implies, protect plants from diseases whose pathogens are in the soil (mould of corn seeds, fusarial wilt and root rots of grain crops, fusarial wilt of flax, black root of beets, root rot of cotton).

With respect to their chemical structure, nature of action, and designation, the fungicides used for seeds and planting stock can be divided into a number of groups (Table 16).

Mercury-containing protectants are distinguished by the universal nature of their protective action, kill the primary infecting organisms on the surface of seeds and in their hulls, but are not effective against internal infection. Mercury formulations, however, are very toxic and dangerous to humans and warm-blooded animals. This restricts their use. Seed protectants not containing mercury include formulations of a various chemical composition. They are less toxic to warm-blooded animals, but are inferior to mercury-containing formulations in the universal nature of their action.

The greatest favour in agricultural practice has been found by thiram. It is highly effective against mould fungi, less effective against bunts and smuts, and has a slight bactericidal action. Thiram penetrates poorly under the hulls of seeds, which is why it is only slightly

Table 16. Classification of Fungicides Used for Treating Seeds and Planting Stock

Group by chemical composition	Fungicides	Crops	Diseases
Mercury-containing substances	Ethylmercury chloride, ethylmercury chloride + chlormequat chloride *, mercurbenzene, mercurhexan **	Wheat, barley oats, rice, castor beans, sugar beets, millet, flax	Common bunt and covered smut of grain, loose smut of millet, pyriculariosis, black root, root rots, mould, fusarial wilts, helminthosporioses
Derivatives of dithiocarbamic acid	Thiram	Grain, except glumaceous, vegetables, pulses, technical, medicinal, planting stock of carrots and onions, potatoes	Smuts, root rots, mould, ascochitosis, black root of beets, blue mould, cercosporosis, phomosis and rots of carrots, all kinds of scab and soft rot of potatoes, neck rot of onions, etc.
Derivatives of oxathiin	Carboxin, carboxin + chlormequat chloride *	Wheat, barley, oats	All kinds of bunt and smut, rust fungi, brown patch
Derivatives of benzimidazole	Benomyl, benomyl + chlormequat chloride	Wheat, barley	Bunt and smut diseases, root rots
		Soybeans, lupine	Root rots
Fungicides of various groups	Oxine-copper, quintozene	Wheat, sugar beets	A set of diseases
		Rye, wheat	Common bunt of wheat, flag smut of rye
	Copper trichlorophenolate, EF-2, EF-2 + chlormequat chloride	Cotton	Bacterial blight
		Wheat, oats, barley	Common bunt of wheat, loose and covered smut of oats, covered smut of barley

	Anilat	Wheat	Loose smut
	Rodan	Rice	Pyriculiariosis
	IBP	Rice	Ditto
	Hymexazol	Sugar beets	Black root, seed mould
	Formalin	Oats, millet, barley	Smuts
	Hexachlorobenzene	Wheat and rye	Common bunt and dwarf bunt
	Metiram, thiram, quintozene, formalin, cuprozin-1, cuprosan	Potatoes	Scab, late blight, brown patch
Combined seed protectants	Fenthiuram **	Vegetables, pulses, corn, flax, cotton	A set of diseases
	Heptathiuram **	Pulses and corn	Ditto
	Tigam **	Pulses, vegetables, corn, buckwheat	Ditto
	EF-2+hexachlorobenzene, EF-2+thiram	Wheat	Common bunt, seed mould
	Carboxin-thiram (carboxin-200)	Wheat, barley	Loose smut, common bunt, covered smut, root rots
	Hexathiuram	Corn, wheat	Mould, fusorial wilt
	Pentathiuram, gammahexane	Wheat, rye	Common bunt of wheat, mould
	Hexachlorobenzene+heptachlor **	Ditto	Common bunt, dwarf bunt

* Substances preventing the lodging of grain crops.
** Substances with an insecticidal activity.

effective as a seed protectant of oat, barley, and millet seeds. Mercury-containing formulations or formalin should be used to treat these seeds.

Hexachlorobenzene and quintozene are used to control external infections with smut and bunt.

Among the group of organic copper-containing formulations, which are distinguished by their strong bactericidal action, copper trichlorophenolate is used. It is 10 times more toxic to the pathogens of bacterial blight of cotton than thiram.

The seed protectant EF-2 is highly effective in controlling the pathogens of seed mould, and also of common bunt of wheat.

Since the fungicides containing no mercury are distinguished by their high selectivity, mixtures of them are recommended to extend their spectrum of action. Formulations are marketed containing thiram with copper trichlorophenolate (fenthiuram), with quintozene and hexachlorobenzene. Copper trichlorophenolate has a good bactericidal action, whereas thiram exhibits a strong fungicidal action, especially against seed mould pathogens. Combined formulations containing thiram and copper trichlorophenolate (fenthiuram, fenthiuram molybdate) protect plants from a set of diseases.

Quintozene is effective against external smut infections, but in increased amounts may inhibit the germination of the seeds and the growth of plants. To diminish its negative effect on plants, a mixture of thiram and quintozene is used. This lowers the danger of harming the plants and expands the spectrum of fungicidal action. An insecticide addition is included in the composition of the mixtures (HCH or heptachlor) to protect the seeds and shoots from soil-dwelling pests, and also to protect the shoots from mandibulate pests during 10 to 14 days after the appearance of the shoots.

The prolonged perennial use of ethylmercury chloride and thiram for dressing wheat seeds against common bunt and root rots may intensify the development of loose smuts.

Of special interest are formulations for disinfection inside seeds. Rodan is used to control loose smut of wheat and rice pyriculariosis.

Promising results in controlling all kinds of bunt and smut, including loose smut, were shown by the systemic fungicide carboxin.

The dressing of seeds in good time with moistening is especially effective. The protectant is retained better on the seeds, the prolonged contact thereof with the seeds intensifies its action and makes it possible to lower the rate of use of the formulation by 20-30% in comparison with preplanting disinfection.

The regular disinfection of seeds makes it possible to reduce the losses due to many diseases (common bunt, covered smut, root rots, cotton bacterial blight, black root of beets, etc.) to virtually imperceptible amounts.

Some of the fungicides described above that are used for the treatment of plants during their vegetation period are also employed for treating seeds and planting stock in addition to the formulations intended only for seed protection.

Benzimidazole derivatives characterized by a broad spectrum of fungicidal action are used for treating the seeds of grain and pulse crops.

Benomyl (a 50% wettable powder) is recommended for dressing the seeds of wheat and barley at rates of 2-3 kg/tonne of seeds against loose and covered smut, and also the pathogens of mould and root rots. To prevent lodging of the crops, treatment with benomyl may be combined with dressing of the seeds with a 60 % solution of chlormequat chloride (six litres per tonne of seeds).

To dress soybeans and lupine, it is recommended to combine treatment with a 50% wettable powder of carbendazim, benomyl (3 kg per tonne of seeds) with nitrogenizing. The treatment with the fungicide is performed not earlier than two weeks before planting, and with the bacterial fertilizer nitragin on the day of planting.

Derivatives of dithiocarbamic acid in addition to quintozene and formalin are used to treat potato tubers against scab, late blight, and brown patch.

Metiram (a 75% wettable powder) is used for treating seed potato tubers at a concentration of 3.7-3.8% and a rate of 70 litre/tonne of tubers. Metiram is also used for treating sugar beet seeds against black root at a rate of 5 kg/tonne.

Cuprozin-1 is used for treating seed potato tubers in a 1% concentration at a rate of the formulation of 0.5-1 kg/tonne.

Cuprozan is used in a 0.5% concentration at a rate of 0.25-0.5 kg of the formulation per tonne of tubers. Seed potato tubers may also be treated with benomyl. For this purpose, a 0.5% suspension is used on the day of planting at a rate of 70 litres per tonne of tubers.

7.12.1. Organic Mercury Compounds

Mercury compounds are mainly used in agriculture for disinfecting seeds.

The introduction of dressing methods with moistening creates more favourable sanitary and hygienic conditions of work.

Mercury-containing formulations are characterized by the universal nature of their fungicidal action, which is due to the mercury itself, and their toxicity is determined by the amount of mercury in a formulation and by how rapidly it is evolved from its composition. The fungicidal and bactericidal activity depends on the chemical structure. Organic mercury compounds are substantially superior to their inorganic counterparts as regards the magnitude of the fungicidal and bactericidal action.

The most active are mixed organic mercury compounds of the general formula RHgX, where R is an aliphatic or aromatic hydrocarbon radical, and X is the residue of an organic or inorganic acid.

Compounds with an aliphatic radical have a stronger fungicidal action, and with an aromatic one—a stronger bactericidal action.

The most active compound containing an aliphatic radical is ethylmercury chloride. Among the aromatic derivatives of mercury, the most active are the phenyl derivatives.

Mercury formulations kill pathogens on the surface of seeds and in their outer hulls, protect against diseases whose pathogens are in the soil, but do not inhibit infections inside seeds (loose smut of wheat and barley).

Mercury-containing compounds inhibit the activity of enzymes and coenzymes, reacting with the sulphhydril groups. In high concentrations, they cause precipitation of the proteins. They transform the basidia and infection hyphae of the pathogen of common bunt of wheat into structureless strands and clots of cytoplasm decomposing on the surface of the tissues of a seed shoot.

Mercury compounds are distinguished by their persistence, and may remain for a long time in biological media without decomposition.

Mercury is sometimes discovered in considerable amounts in water basins, sea animals, fish, and in wild birds, especially those feeding on marine organisms. Mercury compounds may get into vegetable products from the soil, but plants absorb mercury from the soil only in small amounts (0.5-3% of its content in the soil). It is important to note that when mercury-containing formulations are used to dress seeds, not over 3-6 g of mercury are incorporated into the soil per hectare; such small amounts cannot appreciably affect its total balance in the soil even upon its regular use.

The contamination of the environment with mercury is mainly due to the growing amount of industrial waste containing mercury.

Mercury formulations are decomposed in the soil with the liberation of metallic mercury under the influence of microorganisms, and also when subjected to the action of heat or intensive light. Depending on the properties of the soil, they decompose during from one to four months. Mercury is detected in the soil in the form of its oxide or sulphide, one of the least toxic compounds both for microorganisms and for animals, and that is not absorbed by plants.

Mercury formulations are strong poisons to humans and warm-blooded animals. They are volatile and can penetrate into an organism via the respiratory organs. They are characterized by material cumulation. Mercury can accumulate in an organism gradually, concentrating in the brain and spinal cord, the lungs, liver, kidneys, on the walls of the stomach, intestines, causing acute or chronic poisoning. No residues of mercury-containing compounds are tolerated in food products.

Poisoning may occur when working with mercury-containing formulations without reliable means of protection, upon violation of the rules for the storage and transportation of mercury-containing formulations, when using dressed seeds as fodder, and when partaking of the meat of poultry that was fed on dressed grain.

The hazard of poisoning by mercury formulations can be diminished in a variety of ways:

by treating seeds with organomercury formulations with moistening, which reduces the entry of mercury into the breathing zone of the workers from 2 to 9 times;

by using mercury-containing formulations having a lower volatility and toxicity to warm-blooded animals than ethylmercury chloride;

by producing combined protectants containing one-half of the mercury that ethylmercury chloride contains (mercurhexan, mercurbenzene); by producing ethylmercury chloride with the addition of dyes (such seed protectants, when the grain is moistened, colour it to various signal colours indicating that the grain has been treated); the dyeing additions used with ethylmercury chloride include rodamine-C (2%), the zinc salt of methyl blue (2.5-4%), and basic violet (1%);

by introducing special restrictions in the use of mercury formulations (particulary, by prohibiting the treatment with mercury-containing compounds of the seeds of sunflowers, peas, beans, soybeans, chick peas, feeding beans, peanuts, the seeds of all vegetable, cucurbit, medicinal, and ornamental plants). It is recommended to use mercury-containing formulations for disinfecting the seeds of wheat, barley, oats, millet, rice, sugar beets, flax, and castor beans.

Ethylmercury Chloride (Granosan)

The active ingredient, ethylmercury chloride (C_2H_5HgCl), forms white crystals melting at 198 °C. It is moderately soluble in water, and well soluble in organic solvents. It is a quite stable substance, but has a high volatility, reaching 12 mg/m^3 at 20 °C. Strong oxidizing agents decompose it with the formation of inorganic mercury compounds, while reducing agents lead to the formation of diethyl mercury and metallic mercury.

Ethylmercury chloride is marketed in the form of a powder on talc containing 1.8-2.3% of the active ingredient with the addition of dyes and industrial oil.

The formulation can be stored in containers in good order up to 10 years, while in open and faulty containers it rapidly loses its toxicity owing to its high volatility. Ethylmercury chloride is a contact protective and curative fungicide. Its fungitoxicity also manifests itself when its vapour acts on pathogens.

Ethylmercury chloride is used for dressing wheat seeds against common bunt, flag smut, fusorial wilt, and helminthosporiosis, millet seeds against loose smut, rice against pyriculiariosis, fusorial wilt, and helminthosporiosis, oats against smut, castor beans against dry rot, flax against anthracnose, mottling, and escochitosis, and sugar beets against black root.

The rate of use for grain and flax is 1-2 kg/tonne of seeds, and for sugar beets is 2-4 kg/tonne (Table 17). The seeds are treated by dry dressing or with moistening, except for flax seeds. In dry dressing, the seeds do not acquire a signal colour.

Table 17. Application of Ethylmercury Chloride

Crop	Disease	Rate of use of formulation, kg/tonne
Barley	Covered smut, root rots	1.5-2
Castor beans	Fusarial wilt, macrosporiosis, bacteriosis	2
Flax	Anthracnose, ascochitosis, mottling, polysporiosis, fusarial wilt	1.5
Millet	Loose smut	1
Oats	Loose and covered smut, fusarial root rot	1.5-2
Rice	Pyriculiariosis, fusarial wilt, bacteriosis	2
Rye	Flag smut, fusarial and helminthosporiosal root rots	1-2
Sugar beets	Black root of shoots, blue mould, cercosporosis	2-4
Wheat	Common bunt, root rots, mould	1-2

The effectiveness of dressing increases when additions are used such as sulphite-alcohol slops, silicate glue (150-200 g/tonne of seeds), and OP-7 (100-200 g/tonne). Two forms of sulphite-alcohol slops are used: a liquid concentrate (0.7-1 kg/tonne of seeds) and a solid concentrate of slops (0.5-0.7 kg/tonne). The best practice is to dress the seeds in good time (from one to three months prior to planting). If the moisture content of the seeds exceeds 16%, however, mercury-containing formulations may be used not earlier than two or three days prior to planting.

Dressed seeds evolve mercury vapour, therefore they must be stored in special well aired premises.

When treated grain is being poured into sacks, a high concentration of organomercury compounds (0.57-0.85 mg/m^3) is created in the workers' zone of respiration. For this reason, all work must be performed with the use of RU-67 respirators having cartridges "G", overalls made from moleskin, rubber gloves, and special boots; protective goggles PO-1 with a half-mask are used to protect the eyes.

Mercury compounds are absorbed in considerable amounts by the skin and various materials. Among the substances used for demercurization are a 20% solution of iron(III) chloride, a 0.2% solution of potassium permanganate, and Peregood paste (a mixture of pyrolusite and 5% hydrochloric acid in the ratio 1 : 2).

It is prohibited to use dressed grain for any food purposes and for feeding to cattle or poultry. No treatment (washing, cooking, grinding, and the like) frees dressed grain from residues of the protectant. The use of such grain and the products of its processing in food may cause serious poisoning and often death. Ethylmercury chloride is a strong poison to humans and warm-blooded animals (LD_{50} for rats is 30-50 mg/kg). It accumulates in an organism and has an acute chronic toxicity. No residues of ethylmercury chloride are tolerated in food and forage. The maximum tolerated concentration in the air of the working zone is 0.005 mg/m^3, in atmospheric air—0.003 mg/m^3, and in water basins supplying potable water—0.0001 mg/litre.

7.12.2. Combined Mercury-Containing Formulations

These formulations are produced to reduce the use of mercury without diminishing the effectiveness of the formulation and of plant protection not only against diseases, but also against pests. For this reason, the insecticide HCH is added to them. Combined protectants should be used from three to six months before planting the seeds. Upon more prolonged storage of dressed planting stock, diminishing of its germination is possible.

The safety measures and restriction in using combined mercury-containing formulations are the same as for ethylmercury chloride.

Mercurbenzene

It contains 1 part of ethylmercury chloride to 20 parts of hexachlorobenzene. The reduction of the ethylmercury chloride content in the formulation is compensated by the introduction of hexachlorobenzene less toxic to warm-blooded animals, therefore the effectiveness of mercurbenzene in controlling a number of diseases is not lower than that of ethylmercury chloride. It is recommended for dressing seeds of wheat, barley, oats, rye, and millet at a rate of 1.5-2 kg per tonne of seeds.

Mercurhexan

It contains 1 part of ethylmercury chloride to 20 parts of hexachlorobenzene and 12 parts of lindane. It is a seed protectant with universal action.

It is effective against the same pathogens as ethylmercury chloride. Owing to the insecticide addition, it protects the seeds and shoots from damage by wireworms.

It is recommended for dressing the seeds of wheat, rye, oats, barley, flax, and millet.

The rate of use is 1-2 kg per tonne of seeds.

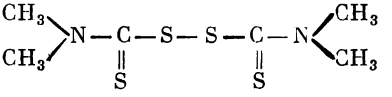
Ethylmercury Chloride + Chlormequat Chloride

The combined use of ethylmercury chloride and the retardant chlormequat chloride protects plants against harm by pathogens and prevents the lodging of grain crops. The seeds of wheat and barley are treated simultaneously with ethylmercury chloride in an amount of 1-2 kg/tonne and with a 60% solution of chlormequat chloride in an amount of 6 litre/tonne.

7.12.3. Seed Protectants Containing No Mercury

Thiram (TMTD, Arasan, Nomersan)

The active ingredient is bis-(dimethylthiocarbamoyl) disulphide (or tetramethylthiuram disulphide):



It forms colourless crystals melting at 155-156 °C. It is virtually insoluble in water (30 mg/litre at room temperature), is slightly soluble in ethanol and diethyl ether, and soluble in acetone and chloroform. It is chemically stable and does not decompose in acid or alkaline media. It is stable to the action of high temperatures. It is decomposed by strong oxidizing agents with the formation of sulphuric acid and carbon dioxide; reducing agents in an alkaline medium transform tetramethylthiuram disulphide into dimethyldithiocarbamates.

It is not volatile, therefore antidust respirators may be used when working with it.

Thiram is marketed in the form of an 80% wettable powder. It is stable in storage. It creates explosive mixtures with air in the form of a fine suspended dust.

Thiram is stable to the action of environmental factors and relates to persistent pesticides that are decomposed in biological media to non-toxic components in the course of 0.5-2 years.

It persists on plants 1-1$^1/_2$ months after treatment. In connection with the danger of residues of the formulation accumulating in the

harvest, thiram is allowed to be used only for dressing seeds and disinfecting planting stock.

Seeds are dressed using the dry method or with moistening directly prior to planting or in good time (several months before planting). The seeds of pulse crops are treated when nitrifying them at least two weeks before planting.

The rate of use of the 80% formulation for dressing seeds of grain is 1.5-2 kg/tonne, of sugar beets—5-6, and of pulses—3-4 kg/tonne.

Thiram is less effective than mercury-containing formulations against smut diseases, especially of glumaceous crops, but reliably protects seeds against the pathogens of mould and root rots. It retains its fungicidal activity up to 30 days on dressed grain.

Thiram is employed to control fusarial wilt of wheat, mould of corn seeds, polysporiosis of flax, ascochitosis of peas, black root of sugar beets, etc.

Thiram is effective against diseases of the seed stock of root vegetables and potato tubers. Carrots intended for seeds are treated before placing in winter storage and before planting at a rate of 6-8 kg/tonne.

The dusting with thiram of root vegetables before placing them into storage reduces waste during the storage period from 1.5 to 2 times; repeated treatment in the spring before planting reduces the mortality of plants in the field from 1.5 to 4 times.

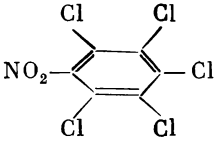
The treatment of potato tubers before planting using a dose of 2.1-2.5 kg of thiram per tonne (70 litres of a 3-3.5% suspension of thiram per tonne) reduces the harm caused by scab, brown patch, and late blight. To control diseases of cabbage, thiram is used for treating the seedlings in hotbeds and nurseries at a rate of 1-1.5 g/m^2. In increased doses, thiram has repellent properties for mice.

Thiram is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 865 mg/kg). It has a pronounced cumulative action, when applied to the skin it causes dermatitis, and when it gets into the eyes—conjunctivitis; it increases the sensitivity to alcohol, and in large doses has a mutagenic and cancerogenic action.

No residues of thiram are tolerated in any food products. The maximum tolerated concentration in the air of the working zone is 0.5 mg/m^3.

Quintozene (PKhNB, PCNB)

The active ingredient is pentachloronitrobenzene:



The chemically pure substance forms colourless crystals melting at 146 °C. It is virtually insoluble in water, and dissolves well in many organic solvents such as benzene, carbon disulphide, and chloroform. The compound has a high chemical stability.

Quintozene is marketed in the form of 25 % and 50 % wettable powders and a 96 % technical product. The 25 % wettable powder is used for dressing the seeds of wheat and rye at a rate of 2 kg/tonne against external infection: common bunt of wheat and flag smut of rye, root rots of shoots, and mould.

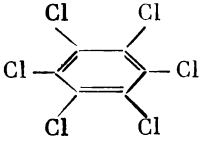
Its pilot application has been recommended for potato seed tubers using a 10 % aqueous suspension (70 litre/tonne). The formulation is allowed only on seed plantings of potatoes to control seed infection by late blight and common scab.

The 50 % wettable powder and the 96 % technical product are used to control cotton wilt by incorporation into the soil in fall ploughing on fields intended for cotton. The rate of use is 100-200 and 50-100 kg/ha, respectively. The formulation is very persistent in the soil.

Quintozene has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 1650 mg/kg), but irritates the mucous membranes. It has pronounced cumulative properties. The maximum tolerated concentration in the air of the working zone is 0.5 mg/m^3, and the tolerance level in grain is 1 mg/kg.

Hexachlorobenzene (HCB)

The active ingredient is hexachlorobenzene:



It forms colourless crystals melting at 226 °C. It is virtually insoluble in water, and well soluble in organic solvents. It is stable in conventional storage conditions, stable to the action of light, acids, and alkalies. Hexachlorobenzene is highly volatile and may have an inhalation effect. The vapour of hexachlorobenzene inhibited the growth of the spores of the common bunt pathogen. It is assumed that the activity of hexachlorobenzene is associated with penetration of the substance into the cells of a fungus. Hexachlorobenzene does not inhibit the growth of the chlamydospores of common bunt of wheat in the soil, but inhibits the pathogen of this disease at the following stages of its development.

Hexachlorobenzene has a high persistence in the soil and in vegetative and animal tissues. Upon penetrating into a coleoptile, it

protects it from infection for a longer time than mercury protectants do.

As a fungicide, hexachlorobenzene is characterized by a narrow selective action. It is effective exclusively against common bunt and dwarf smut of wheat and rye and does not protect the plants from other diseases. This is why it is not used independently, but is employed to prepare combined seed protectants (the formulations mercurbenzene, mercurhexan, gammahexane, and hexathiuram).

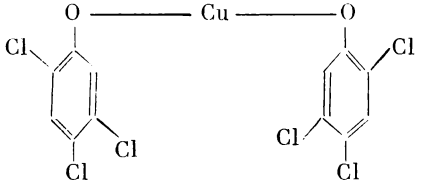
The preplanting and timely use of combined protectants containing hexachlorobenzene does not detract from the germination of seeds. A great effect is achieved in advance treatment because the seeds are disinfected at the expense of the gaseous phase. Hexachlorobenzene has no negative effect on the quality of wheat grain and flour.

Hexachlorobenzene has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 3500-4000 mg/kg), but has an acute chronic toxicity. Persons working with hexachlorobenzene must reliably protect their respiratory organs.

The maximum tolerated concentration in the air of the working zone is 0.9 mg/m^3, and in water is 0.05 mg/litre. The tolerance level in wheat grain is 0.01 mg/kg.

Copper Trichlorophenolate (TKhFM)

The active ingredient is copper 2,4,5-trichlorophenolate:



It is a reddish brown dusty powder with a sharp unpleasant odour. It is virtually insoluble in water, petrol, benzene, and toluene. It dissolves well in ethanol, ether, and dichloroethane. It is stable in storage. In an acid medium, it decomposes to free trichlorophenol, and in an alkaline one, to an alkali metal trichlorophenolate.

Copper trichlorophenolate exhibits a specific activity with respect to the pathogen of bacterial blight of cotton. It is presumed that the bactericidal action of copper trichlorophenolate is a result of its influence on the metabolism processes of bacteria.

The copper of the protectant is used by plants as a microelement.

As a result of seed dressing, the synthesis of chlorophyll was accelerated in cotton and corn shoots, and the intensity of oxidation-reduction processes increased.

Upon its perennial application, copper trichlorophenolate did not accumulate in the soil and had no negative effect on the soil's microflora.

Copper trichlorophenolate is marketed in the form of a 20% powder in a mixture of talc (30%) and kaolin (50%). It contains admixtures of trichlorophenol that impart a specific odour to the formulation.

It is used for the centralized dressing of cotton seeds at ginneries against bacterial blight and root rot. Disinfection may be performed from one to three months prior to planting and directly before planting. The rate of use of the formulation in treatment with moistening is 6, and without moistening, 7 kg/tonne of seeds.

The regular use of copper trichlorophenolate made it possible to virtually completely eliminate the losses of cotton due to bacterial blight.

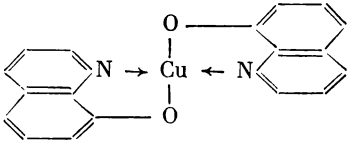
The substance has a high bactericidal activity, which is why it is introduced into the composition of combined formulations (fenthiuram and fenthiuram molybdate).

Copper trichlorophenolate is moderately toxic to humans and warm-blooded animals; it irritates the mucous membranes.

The maximum tolerated concentration in the air of the working zone is 0.1 mg/m^3, and in water is 0.1 mg/litre.

Oxine-Copper (Copper-8-Quinolinolate, Kinolat 15)

The active ingredient is bis-(8-quinolato)copper(I):

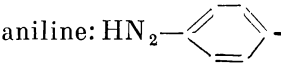


It is a greenish-yellow non-volatile crystalline powder virtually insoluble in water and most organic solvents. It is stable in storage. In an alkaline medium, it decomposes to form copper oxide and an alkali metal quinolate, and in a strong acid—to form a copper salt and 8-hydroxyquinoline or its salt. It has a broad spectrum of fungicigal action and is marketed in the form of a 15% wettable powder.

It is used to treat wheat seeds at 2 kg/tonne and sugar beet seeds at 6 kg of the formulation per tonne of seeds.

Oxine-copper has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 1000-2000 mg/kg). It has a slight irritating action on the skin and mucous membrane.

Rodan

The active ingredient is *p*-rhodananiline: HN_2—  —SCN. It is a cream-coloured crystalline substance melting at 142 °C. It dissolves poorly in water (0.2 g/litre at room temperature) and well in organic compounds.

Rodan is a virtually non-volatile substance. When seeds are dressed, hydrocyanic acid is liberated in the course of damping.

Unchanged *p*-rhodananiline is toxic to the pathogen, while its decomposition products (hydrocyanic acid, *p*-aminothiophenol, and *p*,*p*'-diaminodiphenylsulphide) change the metabolism of plants, increasing their resistance to pathogens and to harm by the barley miner. The acquired resistance is retained for three or four years.

Rodan is marketed in the form of a 25% emulsifiable concentrate. It is used for the moist dressing of rice seeds against pyriculariosis at a rate of 0.23 litre/tonne. Rice seeds are treated once in three years with a 3% solution at a rate of 7.5 litre/tonne of seeds. The latter are then damped for 24 hours, aired, and planted after 48 hours elapse.

Rodan relates to moderately toxic formulations to warm-blooded animals (LD_{50} for rats is 228 mg/kg).

Formalin

The active ingredient is formaldehyde (methanal): $O{=}C\begin{matrix}H\\H\end{matrix}$.

Formaldehyde is a colourless gaseous substance with a pungent irritating odour boiling at —21 °C. It dissolves well in water, ethanol, and diethyl ether. Formalin is an aqueous solution of formaldehyde. Upon prolonged storage, especially in open containers, at a low temperature, formalin polymerizes, as a result of which the solution becomes turbid, and a white gelatinous precipitate of the polymerization products is formed. Such a substance is not fit for use, it may have a harmful effect on the dressed seeds (lowering of their germination). To prevent and retard polymerization, formalin should be diluted with water to half its original concentration, and stored in hermetically sealed dark glass containers in a heated room.

Polymerized formalin may be used only after depolymerization. Should a solution become turbid, its properties are restored by heating. Upon greater polymerization attended by the abundant precipitation of a gelatinous substance, the formalin is diluted with warm water in which caustic (2 g per litre of formalin) or crystalline (12 g per litre of formalin) soda is dissolved. The precipitate will vanish in a few days. A 5-10% solution of soda ash may also be used, adding 50 g per 100 litres of 40% formalin. In this case, the precipitate vanishes in one day.

Depolymerized formalin is used with a view to the solutions having been diluted in depolymerization.

Formaldehyde has contact, fungicidal, and bactericidal action, and is used for disinfecting the seeds of glumaceous plants. It is effective in controlling infection on seeds, but does not protect the latter from being harmed by soil-dwelling microorganisms.

The toxic action of formalin is associated with the irreversible reactions of formaldehyde with the aminogroups of the metabolites. It precipitates proteins and changes the physicochemical properties of cytoplasm.

Formalin is marketed in the form of a 40% aqueous solution of formaldehyde containing 10% of methanol (retarding the polymerization of the formaldehyde), acetone, formic acid, and iron salts.

It is used for the wet and semidry dressing of seeds, incorporation into the soil, and disinfection.

The wet method is used to treat millet seeds strongly infected with loose smut, and the semidry—to treat oat seeds infected with covered and loose smut, and barley seeds infected with covered smut.

In the wet method of dressing, a 0.33% working solution of 40% formalin (0.13% with respect to the active ingredient) is prepared. The seeds are submerged for five minutes into the solution used at a rate of 100 litres per tonne of seeds, next the moist seeds are kept under a film for two hours. The working solution may be used only for a single treatment.

Semidry treatment of seeds is performed with a 1.25% solution of 40% formalin (0.5% with respect to the active ingredient), using 30 litres of the working solution per tonne of oat seeds and 15-20 litres per tonne of barley seeds. After treatment, the moist seeds are kept under a film for 2-4 hours. The seeds are dried in the shade with airing and shovelling (when seeds are dried in the sun, the formaldehyde on their surface polymerizes, which may reduce their germination).

Seeds are treated with formalin not later than 3-5 days, and tobacco seeds not later than 2-3 days before planting, otherwise the germination of the seeds diminishes. When formalin is used properly, the germination of the seeds does not lower, and normal growth and development of the plants are not disrupted.

Formalin is used only to a limited extent in connection with the time-consuming nature of treatment and the possibility of lowering the germination of the seeds.

When it is necessary to disinfect implements, containers, vegetable store cellars, and storage rooms, they are treated with a 2% solution of formalin at a rate of 1 litre/m^2.

Good results are obtained by the aerosol disinfection of the structural members of greenhouses with a 40% aqueous solution of formalin (40-50 litres per 1000 m^2) using an aerosol generator AG-UD-2.

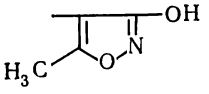
Formalin is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 424 mg/kg). Gaseous formaldehyde irritates the eyes and mucous membrane of the respiratory tracts, affects the skin, and may cause chronic poisoning.

Workers using formalin must protect their skin and respiratory tracts with an industrial filtering gas mask of Grade A.

The maximum tolerated concentration in the air of the working zone is 0.5 mg/m^3, and in water basins is 0.5 mg/litre.

Hymexazol (Hydroxyisoxazole, Tachigaren)

The active ingredient is 3-hydroxy-5-methylisoxozole:



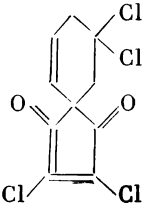
It forms colourless needle-like crystals melting at 86-87 °C. The solubility in water is 85 g/litre at 25 °C. It is well soluble in methanol, ethanol, and acetone. It is stable in acid and alkaline media.

It is marketed in the form of a 70% wettable powder. The fungicide is effective in controlling soil infection, is readily sorbed and migrates in plants. It is recommended for dressing sugar beet seeds in an amount of 6 kg/tonne against black root of the shoots. According to the results of state tests in 1974, hymexazol was approximately twice as effective as thiram against black root of sugar beet shoots. It facilitated a considerable increase in the density of the shoots and lowered the infection by black root from 2.5 to 4 times, which resulted in an increase in the yield by 1.1-1.5 tonnes per hectare and the yield of sugar by 250 kg/ha. The dressing of pelleted seeds with hymexazol was especially effective.

Hymexazol has a low toxicity to humans and warm-blooded animals (LD_{50} for rats when ingested orally is 2723 mg/kg).

EF-2

The active ingredient is 3,3-dichlorobicyclo-(2,2,1)-hept-5-ene-2-spiro-[2′-(4′,5′-dichloro-4′cyclopentene-1′,3′-dione)]:



It is a yellow crystalline powder melting at 129-131.5 °C. It dissolves in acetone.

EF-2 is a fungicide effective against common bunt of wheat, loose and covered smut of oats, covered and black (false) loose smut of barley, root rots and various pathogens of seed mould, especially if they are from the genera *Fusarium* and *Alternaria*.

In its effectiveness against various mould and pathogen fungi, EF-2 is comparable with ethylmercury chloride, but is inferior to it in its fungicidal activity against root rots.

EF-2 has a positive influence on the plants being protected.

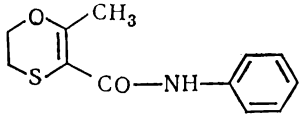
It is marketed in the form of a 50% wettable powder. It is recommended for treating the seeds of wheat, oats, and barley before planting. The seeds are treated with a suspension or with moistening at a rate of use of the fungicide of 3 kg/tonne.

It is recommended to use EF-2 together with chlormequat chloride for treating wheat and barley seeds to protect the plants from the pathogens of mould, smut, bunt, and to prevent lodging of crops. The treatment is performed simultaneously with EF-2 (3 kg of a 50% wettable powder per tonne of seeds) and chlormequat chloride (6 litres of a 60% solution per tonne of seeds).

EF-2 has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 3250 mg/kg).

Carboxin (DCMO, Vitavax)

The active ingredient is 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiin:



It has two crystal structures that revert to one in solution. Structure A melts at 91.5-92.5 °C, and B at 98-100 °C. Their fungicidal activity is identical. The active ingredient dissolves only slightly in water (170 mg/litre at 25 °C), benzene, ethanol, acetone, methanol, and dimethylsulphoxide. It decomposes under the action of strong acids and bases.

Carboxin is a systemic fungicide. It is effective against all kinds of bunt and smut, and also against rust fungi and brown patch on various crops. When the seeds germinate, it penetrates into them and inhibits internal infection. It can migrate in an acropetal direction, protecting the shoots against infection by certain soil-dwelling phytopathogens.

Carboxin is only slightly effective against the pathogens of seed mould, septoria spot, and the root rots of cereal crops, therefore combined formulations are used that in addition to carboxin contain oxine-copper, thiram, etc.

The fungicidal activity of the formulation is due to its ability to accumulate in separate parts of plant cells and disrupt vital processes in fungi.

In the environment, carboxin lends itself more readily to transformations than benzimidazole derivatives. In the soil, it usually decomposes completely in three weeks.

In water and biological media, carboxin is oxidized to the nonfungitoxic sulphoxide and sulphone. The determination of the content of carboxin and its metabolites in barley and wheat plants grown from seeds treated with the fungicide showed that the maximum amount of unchanged carboxin was contained in plants in the third week after planting, while residues were detected in the course of six weeks. The products of transformation of carboxin consisted of 90% of the sulphoxide and 10% of the sulphone obtained as a result of oxidation of the carboxin.

At the early stage of development, the main product of transformation of carboxin in shoots of barley from seeds treated with it was a metabolite para-hydroxylated in the ring. Carboxin is hydrolyzed to aniline and acid in bean plants, and is not hydrolyzed in wheat and barley. No residues of carboxin were detected in the harvest.

Carboxin is marketed in the form of a 75% wettable powder and is used for dressing wheat seeds at a rate of 2.5-3 kg/tonne and barley and oat seeds at a rate of 3-3.5 kg/tonne.

The treated seeds before planting must be kept at least four days in sacks or in piles. When seeds are stored up to two months, the effectiveness of treatment and the germination of the seeds do not change. To prevent lodging of the crops, a 60% solution of chlormequat chloride in an amount of 6 litre/tonne is added to carboxin in dressing the seeds.

Carboxin has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 3200 mg/kg). Carboxin metabolites are rapidly excreted from an animal's organism with the urine.

7.12.4. Combined Seed Protectants

Fenthiuram

Fenthiuram contains 40% of thiram, 10% of copper trichlorophenolate, and 15% of lindane. It decomposes in the soil in 30-40 days, does not accumulate, and has no negative influence on the soil's fertility.

The formulation is effective against mould fungi, bacterial diseases, and protects seeds and shoots from harm by soil-dwelling pests. It is used for dressing the seeds of vegetable and leguminous crops, corn, sugar beets, cotton, sunflower, sorghum, buckwheat, hemp, jute, ambary, sainfoin, perilla, lallemantia, oil-bearing poppy, and medical nightshade.

The rate of use of fenthiuram in treating cotton seeds against bacterial blight and root rot is 10-12 kg, against seed decay is 12 kg, in treating peas and beans against seed mould and root rot is 4-6 kg/tonne of seeds. The rate for other crops is 2-4 kg/ha.

Fenthiuram-Molybdate is fenthiuram with 4% of ammonium molybdate added. It is used for treating the same crops and in the same amounts as fenthiuram, the plants being provided with the microelement molybdenum.

Fenthiuram is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 592 mg/kg).

Thiram + Heptachlor (Heptathiuram)

This is a combined formulation containing 40% of thiram and 20% of heptachlor. It is intended for protecting the seeds of corn (2-4 kg/tonne), peas, soybeans, mung and fodder beans (4-6 kg/tonne), beans, lentils, chick peas, lupine, vetch, peavines, and clover (3-4 kg/tonne). The seeds of leguminous crops with nitrification are treated at least two weeks before planting.

Tigam

Tigam is a combined seed protectant containing 50% of thiram and 20% of lindane. It is used for dressing seeds against a set of diseases and soil-dwelling pests.

Tigam is used to treat the seeds of corn, buckwheat (2 kg/tonne), flax (3 kg/tonne), vegetable crops, beans, lintels, vetch, lupine, chick peas, peavines, clover (3-4 kg/tonne), peas, soybeans, mung and fodder beans (4-6 kg/tonne), and sugar beets (5-6 kg/tonne). The seeds of leguminous crops with nitrification are treated at least two weeks before planting.

Gammahexane

This is a combined formulation containing 30% of hexachlorobenzene and 20% of lindane. It is used for protecting wheat and rye seeds against common bunt and soil-dwelling pests. The rate of use is 2-4 kg/tonne of seeds.

Hexachlorobenzene 30% + Heptachlor 20%

It is used, like gammahexane, for dressing wheat and rye seeds. The rate of use is 2 kg/tonne of seeds.

EF-2 + Hexachlorobenzene

This combined seed protectant is marketed in the form of a 55% wettable powder.

It is recommended for dressing wheat seeds before planting to control common bunt and root rots. The rate of use is 3 kg/tonne of seeds.

EF-2 + Thiram

This combined formulation is marketed in the form of a 64% wettable powder.

It is used to treat wheat seeds at a rate of 3 kg/tonne of seeds.

Hexathiuram

Hexathiuram includes 50% of thiram and 30% of hexachlorobenzene. It is used to treat wheat seeds (2 kg/tonne) and corn seeds (3 kg/tonne).

Pentathiuram

This combined seed protectant contains 20% of pentachloronitrobenzene and 30% of thiram. It is used for dressing wheat and rye seeds against a set of diseases at a rate of 1.5-2 kg/tonne of seeds.

Vitavax-200 (Carboxin + Thiram)

Vitavax-200 is a combined seed protectant formulated as a 75% wettable powder prepared by mixing 75% carboxin and 80% thiram in a proportion of 1 : 1.

Vitavax-200 is effective against common bunt of wheat, loose smut and mould of wheat and barley, lowers the infection of shoots by root rots, and has a positive effect on the field germination and thickness of stand of the crops. The rate of use is 3 kg/tonne of seeds.

7.13. Fungicides Used for Eradication Sprayings, Incorporation into the Soil, and Disinfection

The formulations used for eradication sprayings, incorporation into the soil, and disinfection were described on earlier pages and relate to various groups as regards their chemical structure (Table 18).

Table 18. Classification of Fungicides Used for Eradication Sprayings, Incorporation into the Soil, and Disinfection

Application	Formulations	Features of use	Diseases
Eradication sprayings	DNOC, nitrafen, blue vitriol, green vitriol	Treatment of dormant plants (in autumn or spring)	Scab and brown rot of apple and pear trees, clusterosporiosis, moniliosis, and coccomycosis of stone fruits, grape mildew, gray rot of strawberries, diseases of gooseberries and raspberries
Incorporation into soil	Metam-sodium, dazomet	Incorporation into soil not later than 20-30 days before planting seeds or transplantation of seedlings	Cabbage clubroot and wire stem, white rot and fusarial wilt of cucumbers and tomatoes
	Sulphur, benomyl	Incorporation into soil of hotbeds and nurseries 3 days before planting seeds or picking out seedlings. Watering of soil when planting seedlings in field	Wire stem of seedlings and cabbage clubroot
	Quintozene, chloropicrin	Disinfection of soil at disease seats up to 200 m^2 in area	Potato cancer
	Quintozene, benomyl	Incorporation into soil in fall ploughing on fields earmarked for cotton	Cotton wilt
Disinfection	Formalin	Treatment of containers, storage premises, racks, etc.	Set of diseases

They are employed for exterminating wintering infections of fruit and berry crops, for controlling the most dangerous diseases of plants whose pathogens are in the soil and retain their vitality for a prolonged period (potato cancer, cotton wilt, cabbage clubroot), for disinfecting containers, storage premises, racks, carpet strips in greenhouses to prevent the spreading of infection, and also for sterilizing the soil in sheltered ground.

7.13.1. Fungicides for Eradication Sprayings

The aim of eradication sprayings is to exterminate the wintering stages of plant disease pathogens remaining on fallen leaves, on tree branches and trunks, and on the soil (apple and pear scab, clusterosporiosis and coccomycosis of stone fruits, grape mildew, etc.). DNOC and nitrafen are used for eradication sprayings (Table 19).

Table 19. Use of DNOC and Nitrafen

Crop	Disease	Rate of use, kg/ha	
		DNOC	Nitrafen
Apple and pear trees	Scab, other spots, moniliosis	15-20	40-60
Currants	Anthracnose, septoria spot	8-15	30-40
Gooseberries	Anthracnose, septoria spot, rust	8-15	30-40
Grapevines	Anthracnose, cercosporosis, mildew, oidium, spot necrosis	20	40-60
Raspberries	Anthracnose, rust	—	30-40
Stone fruits	Clusterosporiosis, coccomycosis, other spots, moniliosis, curliness	10-20	40-60
Strawberries	Gray and brown spots	—	20-30

These are pesticides with complex action having fungicidal, insecticidal, and herbicidal properties. Their effectiveness is determined by the thoroughness and uniformity of treatment. The working liquid is customarily used at a rate of from 800 to 3000 litre/ha depending on what is being treated. Spraying is performed in the autumn, or in the spring before opening of the buds. These formulations must never be used for eradication sprayings during the vegetation period because they have substantial phytocidal properties.

The eradication of the wintering stages of pathogens lowers the infection of plants in the spring, when shoots grow, leaves form, and the development of diseases is especially dangerous. Eradication treatments inhibit the spreading of diseases during the entire vegetation period, which excludes blue spraying with Bordeaux mixture and makes it possible to diminish the number of sprayings during the vegetation period of plants.

DNOC is employed in a 1% concentration for spraying orchards and grapevines (8-20 kg/ha of the formulation). Spraying is performed in the early spring (before the beginning of bud opening) at an ambient temperature not over 20 °C, or in the autumn (after falling defoliation). The trees are treated, and also the soil in the zone of the circles around the trunks and in the inter-row spacings. After

treatment, the inter-row spacings should not be cultivated and the circles around the trunks should not be ploughed. At a temperature below 13 °C, the activity of DNOC diminishes. At elevated temperatures, it rapidly evaporates from treated surfaces. An increased humidity and atmospheric precipitation facilitate the penetration of DNOC into the fruit body of the fungi.

Eradication sprayings with DNOC formulations are effective against anthracnose, mildew, oidium, spotnecrosis of grapes, clusterosporiosis and moniliosis of stone fruits (apricots, peaches, cherries, plums), powdery mildew and septoria spot of gooseberries, anthracnose and septoria spot of currants, and against a set of pests and diseases of apple and pear trees.

The application of DNOC is limited by its high toxicity to humans and warm-blooded animals.

Nitrafen is a less toxic formulation, and is used in higher concentrations (2-3% or 10-60 kg/ha of the formulation) than DNOC. It is effective only upon the abundant and uniform watering of trees and the soil. It is used for eradication sprayings against apple and pear scab, grape mildew, diseases of stone fruits (apricots, plums, peaches, and cherries—40-60 kg/ha) and berries (currants, gooseberries, raspberries—30-40 kg/ha).

Table 20. Use of Blue and Green Vitriol

Crop	Diseases	Concentration, way and period of treatment
	Blue Vitriol	
Apple and pear trees	Bacterial bark cancer	1%, disinfection of wounds after dressing
	Root cancer	1%, disinfection of root system of sets
	Scab, various spots, moniliosis, desiccation	1%, spraying before opening of buds
Stone fruits	Clusterosporiosis, coccomycosis and other spots, moniliosis, curliness	1%, spraying before opening of buds
	Green Vitriol	
Grapevines	Anthracnose, spot necrosis, mildew, bacterial cancer	2-3%, spraying of plants and soil under them before beginning of vegetation and after vegetation
Pip fruits	Diseases of trunk and branches, scab, other spots, moniliosis, cancer	2-3%, spraying in spring (before beginning of vegetation) or in autumn (after vegetation)

Strawberries are treated in the spring (before the leaves begin to grow) with a 1.5-2% solution of the formulation at a rate of 20-30 kg/ha.

Blue and green vitriols are also used for eradication sprayings (Table 20).

In the early spring (when plants are dormant before opening of the buds), treatments may be performed with a 1% solution of technical 98% **blue vitriol**. The rate of use of blue vitriol for treating apples and pears is 15-20, apricots, peaches, plums, and cherries is 10-15, and gooseberries and currants is 8-10 kg/ha. Blue vitriol is effective against scab, brown rot, a set of diseases of stone fruits and berries, and exterminates mosses and lichens.

A 53% soluble powder of **green vitriol** is also used for eradication sprayings of apple and pear trees. Spraying is effective against fungal disease, mosses, and lichens. Plants are sprayed before vegetation, and after vegetation with a 2-3% solution at a rate of 30-40 kg/ha of the formulation.

Green vitriol must never be used together with other pesticides.

7.13.2. Fungicides for Incorporation into Soil

Soil fungicides are formulations used to disinfect the soil from hamrful microorganisms and the pathogens of such diseases as clubroot of cabbage, wire stem of seedlings, white rot and fusarial wilt of cucumbers and tomatoes, and verticilliaceous wilt of cotton.

The substances in greatest favour for disinfecting the soil are metam-sodium and dazomet (see Sec. 6.6). They are characterized by a strong eradicating action, have no selectivity, and inhibit fungi, bacteria, harmful insects, and weeds. Metam-sodium and dazomet are also toxic to cultivated plants, therefore a period sufficient for the loss of phytotoxicity (30-50 days) must elapse after incorporation of these substances into the soil before planting.

Soil fungicides are applied by watering the soil with aqueous solutions or suspensions of the formulations, while powders are mixed with sand or soil and uniformly dispersed over the surface being treated.

The rates of use of metam-sodium and dazomet depend on the pathogens, the soil temperature, and the conditions of incorporation. For example, in controlling wire (black) stem of cabbage, the lodging of cucumbers, white rot of cucumbers and tomatoes, metam-sodium is effective at a soil temperature up to 12 °C in an amount of 75-100 ml/m^2 at a temperature up to 20 °C, of 50-75 ml, and at 20-22 C°, 25-50 ml/m^2; in controlling cabbage clubroot and the wilt of cucumbers and tomatoes, metam-sodium is effective at a soil temperature up to 12 °C in an amount of 175-300 ml/m^2, up to 20 °C, 150-300 ml, and at 20-22 °C, 125-300 ml/m^2. It is recommended to

use metam-sodium for controlling root rots of tobacco (750-1000 kg/ha), for controlling root rots, fusarial and verticillaceous wilt of cucurbit and nightshade crops (2000 kg/ha), for controlling clubroot, wire stem, and fusarial wilt of cabbage (750-1750 kg/ha). It is incorporated into the soil not later than 30 days before planting the seeds or transplanting the seedlings.

Metam-sodium is promising for disinfecting the soil in greenhouses and hotbeds against a group of soil pathogens. For sterilizing soil mixtures, metam-sodium is used at a rate of 1 kg/m^3, from 30 to 50 days before planting.

Disinfection of the soil accelerates the growth and development of plants, facilitates the earlier ripening of the crop, and increases the taking root of plants after seedlings are transplanted into the soil.

Dazomet is recommended for controlling a number of soil pathogens of cabbage and other cruciferous crops by incorporating into the soil 400-1400 kg/ha not later than 20 days before planting the seeds and transplanting the seedlings, and also for controlling a group of pathogens of cucurbit, nightshade, and ornamental crops by incorporation into the soil at a rate of 1500 kg/ha not later than 30 days before planting seeds or seedlings.

The incorporation of fungicides into the soil is promising not only to control diseases of plants in greenhouses, but also in open soil when cultivating cotton and at seats of potato cancer.

To control wire stem and diseases of cabbage, zineb or sulphur at a rate of 5 g/m^2 or metiram at a rate of 3-5 g/m^2 is incorporated into the soil three days before planting the seeds or singling the shoots. When transplanting cabbage seedlings, zineb, sulphur, or benomyl is introduced by watering the soil simultaneously with planting. For this purpose a 0.25-0.3% suspension of zineb (20-25 kg/ha of the formulation), a 0.4-0.45% suspension of colloidal sulphur (30-40 kg/ha of the formulation), or a 0.1-0.15% suspension of benomyl (10-12 kg/ha of the formulation) is prepared.

This treatment diminishes the infection of cabbage by clubroot.

The row method of incorporation of fungicides into the soil in the conditions of the Leningrad region lowered the number of plants with major infection by clubroot by 15-25% and more and increased the cabbage yield by 6-14.5 tonne/ha. Every rouble spent on clubroot control brought in 30-60 roubles of profit.

The soil is treated with nitrafen and chloropicrin to control potato cancer.

Nitrafen is incorporated into the soil at a rate of 400-440 g/m^2 for quarantine purposes to eliminate seats of potato cancer on areas not over 0.02 ha in size and not nearer than 200 m to water-supply sources.

Chloropicrin is used to disinfect potato cancer seats on plots not over 200 m^2 in area. The rate of use is 150 ml/m^2. Since chloropicrin

relates to strong poisons, work with it must be performed only under the supervision of specialists. It is prohibited to grow agricultural crops on treated plots during three years.

Quintozene and benomyl are incorporated into the soil to control cotton wilt. They are introduced in fall ploughing on fields intended for cotton. The rate of use of 96% technical quintozene is 50-100 kg/ha, of a 50% wettable powder of quintozene is 100-200 kg/ha, and of a 50% wettable powder of benomyl is 75-150 kg/ha. The systemic fungicides introduced into the zone of the active roots rapidly enter the plants, accumulate mainly in the leaves, inhibit the development of wilt, and do not penetrate into the bolls and seeds.

In various cotton-growing regions, such treatments of strongly infected fields resulted in inhibition of the development of verticilliose from 90-95 to 10-30%.

It is important to note that systemic fungicides incorporated in fall ploughing to a depth of 28-30 cm retained their aftereffect during at least two vegetation seasons.

Chapter 8

HERBICIDES

Herbicides are chemicals employed to kill weeds. The major part of herbicides relate to organic compounds characterized by a high physiological activity and effectiveness at relatively low rates of use. Some inorganic compounds are also used as herbicides.

Depending on their properties, selective and non-selective (Table 21) herbicides are distinguished.

Table 21. Non-selective (Sterilant) Herbicides

For treating green organs of plants		For incorporation into the soil
contact	systemic	
Petroleum oils, DNOC, nitrafen, diquat	Dalapon, 2,4-D, tordon 22K, dicamba, etc.	2,3,6-TBA, tordon 22K, monuron, diuron, fenuron, atrazine, simazine, TCA, diquat, etc.

Non-selective herbicides are used for killing all plants on areas where no plant growth is desired: on the shoulders of highways and railways and on railway tracks, on drainage and irrigation canals, along power transmission lines, on sports grounds, etc.

Selective herbicides kill or inhibit weed growth without harming crop plants. Selective herbicides can be used on plantings of almost all crops.

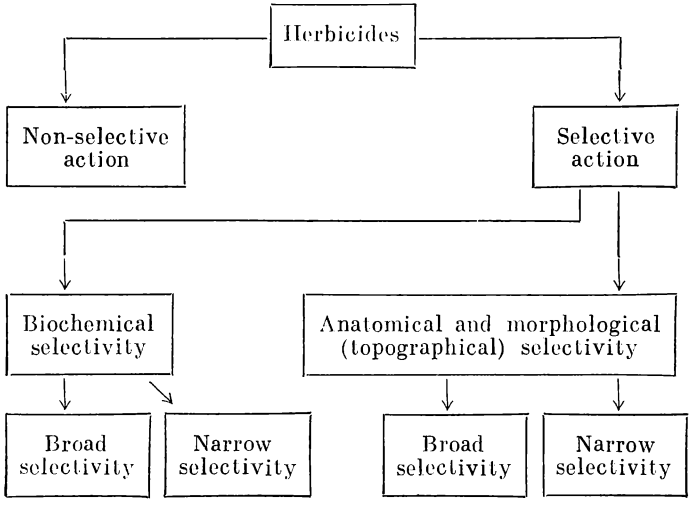
Many weeds can be killed without harming the crop plants upon the proper choice of a herbicide, its rate of use, the time and way of treatment.

Selectivity depends on the anatomical, morphological, and physiological features of the plants, and also on the chemical composition and physicochemical properties of the herbicide and its physiological activity. Many selective herbicides kill a considerable number of weed species. For instance, the herbicides 2,4-D and MCPA eradicate numerous dicotyledonous weeds in grain fields. Derivatives of 1,3,5-triazine—atrazine and simazine—kill many di- and monocotyledonous weeds on corn fields. These are examples of the broad selectivity of herbicides. Conversely, some herbicides kill a very limited number of weed species or even one weed. For example, barban used for treating wheat, barley, pea, and corn fields against wild oats acts on this weed a very short time (only in the stage of one or two leaves). Propanil used to kill Japanese barnyard millet on rice fields has a very weak effect on other weeds.

These are examples of the narrow selectivity of herbicides.

Some other herbicides such as dalapon, TCA, and chlorpropham are also characterized by a narrow selectivity.

The classification of herbicides with a view to their selectivity can be represented by the following block diagram:



Topographical selectivity is due to the differences in the anatomical and morphological structure of plants. For example, plants with dense ground tissues, cuticle, a wax coating, and also with dense nap are more resistant to herbicides because their dense ground tissues prevent the penetration of the herbicides into the plants. Plants with leaves directed vertically upward are also more resistant to herbicides because a considerable part of the herbicide solution drips down from these leaves.

Plants with a deep root system exhibit resistance to soil herbicides. For example, Canadian (creeping) thistle, field sowthistle, Russian knapweed, field bindweed, and common horsetail are resistant to atrazine and simazine because these herbicides remain in the top 10-centimetre layer of soil and do not reach the zone of the active roots. These features explain the use of the above-mentioned herbicides in fruit growing and forest nurseries. They kill many weeds whose roots are concentrated in the top layer of the soil, but do not harm the fruit plants and tree seedlings whose root systems are at a considerable depth.

The resistance and sensitivity of plants to herbicides are associated with biochemical selectivity.

The herbicides penetrating into plants undergo various transformations. In some cases this leads to their decomposition and inactivation, in others, to a greater phytocidal activity. Quite often a considerable part of herbicides penetrating into the leaves are excreted through the root system without harming the plant.

The resistance of some plants to 2,4-D is explained by its decomposition in the plants' organisms.

For example, northern red currants and a number of varieties of strawberries are capable of decarboxylating the side chain of 2,4-D. In gramineous plants, 2,4-D is detoxified by combination of the herbicide with the proteins of the undestroyed cellular structures, the proteins of the cytoplasm membranes, and also by decarboxylation and the formation of complexes with substances of a non-protein nature.

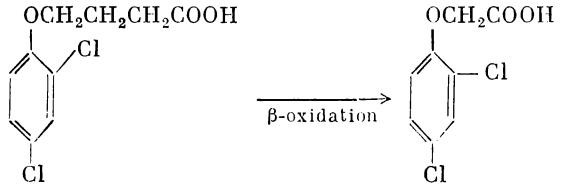
Some weeds resistant to 2,4-D (knotweed, plantain, common chickweed) are also capable of decontaminating the herbicide. In knotweed, this occurs owing to combination of the 2,4-D with the cell proteins, in plantain, owing to combination with substances of a non-protein nature, and in common chickweed, owing to intensive processes of decarboxylation.

The selectivity of 1,3,5-triazine derivatives is associated first of all with the features of translocation of the herbicides and their accumulation at places where phytotoxicity is exhibited. It has been established that resistant and non-resistant plants absorb almost equal amounts of herbicide from its solution, but in resistant species (corn) the largest content of the herbicide is detected in the roots,

whereas in non-resistant plants it penetrates more rapidly and in larger amounts into the photosynthesizing organs, where it exhibits its phytocidal nature. In addition, in resistant plants, simazine and atrazine transform more rapidly into non-phytotoxic compounds, whereas in non-resistant plants they remain for a long time in an unchanged form. In various plants, the products of metabolism of the herbicides differ: in some plants the herbicides rapidly transform into non-phytotoxic hydroxy derivatives; in others the process of dealkylation prevails, as a result of which less phytotoxic products are formed; in third plants, highly polar water-soluble products form.

The decomposition of simazine and atrazine in corn plants occurs both under the action of enzymes, primarily peroxidase, and chemically (under the action of benzoxazine derivatives).

An example of intensification of a herbicide's phytotoxicity is the transformation of MCPB and 2,4-DB, which in plants sensitive to them transform under the action of the enzyme process of β-oxidation into the more phytotoxic MCPA and 2,4-D. For 2,4-DB, we have:

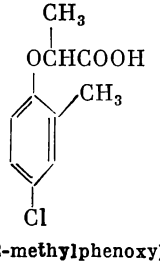


4-(2,4-dichlorophenoxy) butyric acid (2,4-DB)

2,4-dichlorophenoxyacetic acid (2,4-D)

Consequently, plants having a system of β-oxidation are sensitive to MCPB and 2,4-DB, while plants not having this system, conversely, are resistant. For instance, bean crops are resistant to these herbicides, while many weeds attending them are sensitive.

The resistance of some weeds (cleavers and common chickweed) to MCPA is a result of inactivation of the MCPA because of the detachment of both carbon atoms in the side chain. But the same weeds are sensitive to mecoprop because the side chain of the latter's molecule has a methyl group CH_3 preventing the decomposition of the herbicide and its inactivation:



Mecoprop (2-(4-chloro-2-methylphenoxy) propionic acid)

This is why the given herbicide is used to kill weeds resistant to MCPA and 2,4-D and is added to herbicide mixtures for this purpose.

Selective herbicides enter plants in different ways: some via the leaves and move along the vessels of the phloem, while others enter via the roots from the soil solution. This explains why they are applied in different ways: herbicides entering via the leaves are used to spray the green organs of plants, while those entering via the roots are incorporated into the soil. It must be noted that such a division is arbitrary because many herbicides (2,4-D, MCPA, dicamba, picloram, dalapon, etc.) may penetrate into plants via both the leaves and the roots.

All selective herbicides depending on the features of their action on a plant are divided into two groups: contact and systemic (or translocated) herbicides (Table 22).

Contact herbicides kill only the parts of a plant to which they are applied. When considerably harmed, the green organs of plants or young shoots (upon contact with herbicides in the soil) perish, but contact herbicides are not virtually translocated in a plant, hence they do not affect the root system of weeds, and the latter grow again.

Systemic herbicides can move along the vascular system of plants, acting on their entire organisms.

During their translocation within a plant, herbicides are partly inactivated because of reaction with the contents of the cells: absorption by the cells, decomposition by enzymes, and the formation of complexes. The herbicides move along the phloem into the root system, the generative organs, accumulate in the zones of active growth and in the meristematic tissues, which is just where they induce deep disruptions of the physiological processes leading to perishing of the plants.

Herbicides are sucked in with the soil solution by the root hairs, reach the vessels of the xylem, and together with the transpiration stream move into the green organs of plants and accumulate in the leaves.

Systemic herbicides are effective against perennial weeds with a deep root system, and also against shrubs.

According to present-day notions, two systems of absorption and translocation can be earmarked in plants: passive and active absorption. The former occurs with no expenditure of metabolic energy and is induced by the energy of thermal diffusion and the free surface energy used for transpiration. Active absorption and translocation are closely related to metabolism and are mainly induced by the energy of the macroergic bonds of adenasine triphosphate.

The passive absorption system consists of a continuous hydrostatic system of free space and xylem vessels; the active absorption and translocation system consists of the cell protoplasts joined to one another by plasmodesmata.

Table 22. Classification of Selective Herbicides

For treating green organs of plants		For incorporation into soil
contact	systemic	systemic
Mineral oils *Nitrophenols* DNOC, nitrafen, nitrofen *Halogen phenols* Sodium pentachlorophenolate *Aliphatic acid amides and nitriles* Propanil, pentanochlor, propachlor *Oxybenzoic acid derivatives* Ioxynil, actril AS, actril M *Heterocyclic compounds* Diquat	*Aliphatic carboxylic acids* Dalapon *Benzoic acid derivatives* Chloramben, dicamba, 2,3,6-TBA, chlorthiamid, benzoylprop ethyl *Phenoxyalkylcarboxylic acids* 2,4-D (salts and esters) MCPA *Phenoxypropionic acids* Mecoprop *Phenoxybutyric acids* MCPB, 2,4-DB *Carbamic acid derivatives* Phenmedipham, desmedipham, barban *Heterocyclic compounds* MG-sodium, Tordon 22K	*Aromatic amines* Nitrafor, trifluralin *Aliphatic carboxylic acids* Dalapon, TCA *Aromatic carboxylic acids* Diphenamid, chlorthal-dimethyl *Carbamic acid derivatives* Chlorpropham *Thiocarbamic acid derivatives* Tri-allate, pebulate, EPTC, cycloate, molinate, thiobencarb *Urea derivatives* Dichloralurea, fenuron, monuron, diuron, linuron, monolinuron, meturin, chlorbromuron, metobromuron, chlorotoluron, metoxuron, chloroxuron, norea, fluometuron *1,3,5*-triazines Atrazine, propazine, prometryne, simazine, desmetryne, polytriazine, aziprotryne, dipropetryne, terbutryne *Heterocyclic compounds* Lenacil, pyrazon, tordon 22K, metribuzin, terbacil
Combined Formulations (Herbicide Mixtures)		
Aniten C, aniten M, biyalan, dialen, diamet-D, agelon, acetlur, dalur, isolin, cartex M, camparol, diapren, cambilene, SIS-67 MEV, tordon 101, topogard		

8.1. Periods and Ways of Application

When herbicides are to be applied, a specialist must correctly choose the required formulation, set the periods and ways of treating planted fields and the optimal rate of use of the formulation and

liquid (solvent). Even a slight error in establishing the rate of use of a formulation or liquid may lead to excessive expenditure, and often to direct harm.

The periods and ways of herbicide application depend on the properties of the herbicides, their formulations, the ways they enter plants, the selectivity of cultivated plants, and the spectrum of action of the herbicides, i.e. the set of weeds killed.

The application of herbicides in the autumn in combination with fall tillage of the soil is promising for killing perennial offset and rootstock weeds. During this period, many herbicides may be used both by spraying vegetating weeds with systemic and contact formulations and by incorporation of herbicides with larger rates of use because they will become completely inactivated in autumn and winter and will not harm the cultivated plants sowed in the spring. For example, on weedy fields with thistle, field sowthistle, and field bindweed, the amine salt of 2,4-D is used in the autumn after harvesting of the crops at a rate of the 40% formulation of 5-7 kg (2-3 kg a.i.) per hectare. To kill couch grass on fields earmarked for planting flax, potatoes, cabbage, sugar and stock beets, carrots, and cucumbers, autumn spraying of the soil with sodium trichloroacetate is recommended at a rate of use of the 90% formulation of 23-50 kg (20.7-45 kg a.i.) per hectare. Many other herbicides and their mixtures may be used for autumn application.

In preplanting application, herbicides may be used in a mixture with mineral fertilizers, and also by spraying fields with solutions, suspensions, or emulsions followed by incorporation into the soil by cultivation or harrowing. The herbicides kill growing weeds and their shoots.

Herbicides may also be introduced in the form of granules into the drill rows of cultivated plants or in the form of solutions, suspensions, or emulsions into the row-spacings. This way makes it possible to use the herbicides economically with a sufficiently high agrotechnical effect. Before incorporating herbicides, the soil must be well levelled, and the herbicides applied quickly, especially such volatile ones as trifluralin, tri-allate, pebulate, and EPTC.

In preemergence application (after planting and before the appearance of cultivated plant shoots), herbicides are introduced by spraying the fields with solutions, suspensions, or emulsions. The herbicides kill both vegetating and sprouting weeds. Before the emergence of the cultivated plants, herbicides acting in the soil may be used, and also herbicides that are effective in spraying vegetating weeds (contact and systemic).

It must be borne in mind that the time for the preemergence application of herbicides is limited to a few days from planting to the emergence of the crop seedlings, while the herbicides may not be incorporated into the soil by tillage. Consequently, less volatile

substances must be used, and they must be incorporated so that the herbicide solutions get into the moistened layer of the soil. Here larger rates of use of the liquid are needed because in the top dry layer the substances will not be toxic to weeds. This is especially important for herbicides that are derivatives of 1,3,5-triazines.

The preplanting and preemergence incorporation of herbicides is very effective because the herbicides kill the weeds in the earliest stages of development of the cultivated plants when they are the most sensitive to weediness.

Postemergence treatments with herbicides are performed by spraying. Granulated formulations are also used, for example, 10% granulated butyl ester of 2,4-D is recommended for the spring treatment of winter crops simultaneously with top-dressing with ammonium nitrate. This kills the shoots of many weeds, including scentless mayweed.

In the postemergence application of herbicides, it is especially important to properly establish the treatment periods and the rates of use of the herbicides to avoid harming the cultivated plants and to kill the weeds at an early age when they are more sensitive to the herbicides.

In row crops, postemergence directed spraying is practised, when herbicides by means of special sprayers are introduced into the rows or only into the inter-row spacings.

Granulated herbicides are incorporated with the aid of special machines to the required depth, and also into the rows or inter-row spacings, or are dispersed over the surface of the field. Granulated herbicides act longer in the soil, are decomposed more slowly by microorganisms and under the influence of physicochemical processes, and the active ingredient is gradually liberated into the soil solution.

In recent years in regions experiencing wind erosion, herbicides are used on fallow fields to reduce the number of tillages and, consequently, to diminish the dispersion of the top soil layer.

According to data of the All-Union Research Institute of Grain Growing, the use of herbicides on fallow land halved the mechanical tilling of the soil. After two spring tillings of the soil by subsurface cultivators, upon the growth of offset weeds (the middle of June), the field should be sprayed with herbicides 2,4-D, for instance with the amine salt, at a rate of 1.6 kg a.i./ha.

The second chemical treatment of the fallow land is performed in 30 days after the first one, and the field is virtually cleaned of weeds, the soil does not become eroded, has the optimal density, and no erosion processes develop. For the same purpose, it is recommended to treat fallow land two or three times during a season to kill vegetating weeds by means of a 20% aqueous solution of diquat at a rate of 5-10 kg of the formulation (1-2 kg a.i.) per hectare.

Diquat kills both di- and monocotyledonous biennial and annual weeds.

In recent years, the introduction of herbicides together with irrigation water (herbigation) has been used in a number of countries.

On paddy fields with watering by flooding, the herbicide molinate is used in this way, on sugar beet fields when watering along furrows and by sprinkling—cycloate and EPTC. Modern sprinkling systems allow many herbicides to be used with a fertilizer over vegetating plants, and since the dilution of the herbicides with water is very high (1:50 000), their very uniform distribution over the field is ensured.

8.2. Rates of Use

The proper calculation of the rate (dose) of use or application of herbicides is exceedingly important because excessive use may harm the plants and lower the yield, while insufficient use leads to diminishing of the effectiveness of the herbicides in killing weeds, which also results in lowering of the yield and in a growth of weediness.

At present the optimal rates of use have been determined experimentally for all herbicides for application to various crops, as well as the periods and ways of their incorporation.

The rate must be established in each individual case depending on the specific composition of the weeds, the degree of weediness, the mechanical composition of the soil, the content of organic matter in it, and also with a view to the weather conditions when the herbicides are to be applied. Account must also be taken of the possible residual effects of herbicides on following crops in the crop rotation. For example, it is recommended to use atrazine in the form of a 50% wettable powder on corn fields by spraying the soil before planting, when planting, or before emergence of the crop at a rate of 3-8 kg of the formulation (1.5-4 kg a.i.) per hectare. This signifies that the minimum rate (1.5-2 kg a.i./ha) should be used on soils with a light mechanical composition, 2-3 kg a.i./ha on medium and heavy loams, and 3-4 kg a.i./ha and more on chernozem and peat soils with a high content of organic matter and a high absorptivity.

The maximum dose (1 kg a.i./ha) of the herbicide 2,4-D in the form of its 40% amine salt should be used on cereal crops when perennial offset weeds are present, and a dose of 0.6 kg a.i. (1.5 kg of the formulation) per hectare if weeds more sensitive to this herbicide predominate, for instance of the goosefoot family.

Instructions and training aids indicate the rates of use of herbicides in kilograms of the active ingredient per hectare, or in kilograms of the formulation (technical product) per hectare. In a number

of cases, it is more convenient to deal with the rates of use of the herbicides expressed in the active ingredient.

For example, the butyl ester of 2,4-D is marketed in the form of a 72% technical formulation (for aerial spraying) and 32% and 43% emulsifiable concentrates (butapon). In this case, knowing the rate of use of the butyl ester of 2,4-D for grain crops expressed in the active ingredient, equal to 0.3-0.5 kg/ha, or on an average 0.4 kg/ha, it is simple to calculate the rate of use of any of the marketed formulations of the herbicide by the following formula:

$$R = \frac{r \times 100}{p}$$

where R = rate of use of the formulation, kg/ha
r = rate of use of the active ingredient, kg/ha
p = per cent of active ingredient in the formulation.

Using this formula, we can evaluate the rates of use of all the formulations of 2,4-D butyl ester:
72% butyl ester:

$$R = \frac{0.4 \times 100}{72} = 0.56 \text{ kg/ha}$$

32% emulsifiable concentrate of 2,4-D butyl ester:

$$R = \frac{0.4 \times 100}{32} = 1.25 \text{ kg/ha}$$

43% emulsifiable concentrate (butapon):

$$R = \frac{0.4 \times 100}{43} = 0.93 \text{ kg/ha}$$

Knowing the rate of use of a formulation, we can use this formula to determine how much of the active ingredient is needed per hectare:

$$r = \frac{Rp}{100}$$

For example, the rate of use of a 32% emulsifiable concentrate of 2,4-D butyl ester is 1.25 kg/ha. The amount of active ingredient applied will be

$$r = \frac{1.25 \times 32}{100} = 0.4 \text{ kg/ha}$$

In cultivating row crops, the herbicides are applied in bands. Only the rows are sprayed, while the inter-row spacings are cultivated. In this case, the rate of use of a herbicide is smaller, and it is calculated by the following formula

$$R_b = R_o \frac{w}{v}$$

where R_b = rate of use of herbicide in band application, kg/ha
R_o = rate of use in overall application, kg/ha
w = width of sprayed band, cm
b = width of inter-row spacing, cm.

For example, the rate of use of phenmedipham in overall application is 6 litre/ha, the width of the band sprayed is $w = 25$ cm, and the width of an inter-row spacing is 44.5 cm. Hence, $R_b = 6 \times \times \frac{25}{44.5} = 3.37$ litre/ha of the formulation.

In a similar way, the rate of use of a liquid for band spraying is calculated.

8.3. Rates of Use of Solvent

The rate of use of the liquid in which a herbicide is dissolved depends on the nature of action of the herbicide and on the machinery and equipment used. Higher rates of use of the liquid are established for contact herbicides and herbicides acting in the soil. When using tractor mounted and trailer sprayers, the rates of use of the liquid are also higher than for aerial treatments.

Approximate Rates of Use of Liquid

Tractor Sprayers

Contact herbicides	300-600 litre/ha
Systemic herbicides	150-300 litre/ha
Herbicides acting in soil	300-400 litre/ha

Aerial Sprayers

On cereal crops with low-volume spraying (25 litre/ha) upon deterioration of the conditions (lowering of the relative humidity to 50%), the rate of use is increased to 50 litre/ha.

For the application of soil herbicides (simazine, atrazine, dichloralurea, TCA, linuron, etc.), and also for treating rice (propanil, amine salt of 2,4-D)—50-100 litre/ha.

For treating flax fields with MCPA—100-150 litre/ha (higher rates of use of the liquid are established for the maximum doses of herbicides).

In the aerial spraying of desiccants—from 100 to 200 litre/ha.

When working with tractor sprayers, the rate of use of the liquid (solvent) is calculated by the formula

$$Q = \frac{600qn}{tw}$$

where Q = rate of use of liquid, litre/ha
q = outflow of liquid from one nozzle, litre/min
n = number of nozzles
v = speed of tractor, km/h
w = width of spraying, m
600 = conversion factor.

A glance at the formula shows that the rate of use of a liquid (Q) is directly proportional to the outflow of the liquid from one nozzle (q) and the number of nozzles, and inversely proportional to the speed of the tractor (v) and the width of spraying (w).

During work, changes in the rate of use of a liquid must never be tolerated, therefore the speed and the width of spraying must be constant. The outflow of a liquid from a nozzle depends on the diameter of the outlet orifice and the pressure in the sprayer, which must be adjusted to obtain the preset rate of use of the liquid. The outflow of a liquid from one nozzle (q) is calculated by the formula

$$q = \frac{Qvw}{600n}$$

The pressure needed to ensure the required outflow of the liquid from one nozzle can be determined from Table 23.

Table 23. Rate of Flow of Liquid Through Sprayers (litre/min) at Various Pressures

Sprayer		Pressure, kgf/cm²						Machine used
Type	Diameter, mm	0.5	1.0	2.0	3.0	4.0	5.0	
Deflector	1.5	1.1	1.5	2.1	2.6	3.0	3.2	ON-400, POU with rod
Centrifugal	1.5	1.5 0.55	2.0 0.61		2.5 0.70	3.0 0.83		POU in band spraying, accessories
Centrifugal		5	10		15	20		OVT-1a, accessories, rods
N59.010	1.5	1.2	1.6		1.9	2.3		
N59.020	2.0	1.4	2.2		2.5	2.8		
N59.030	3.0	1.9	3.0		3.6	3.8		

In practical work, to achieve the required rate of use of a liquid, in addition to adjusting the pressure, it is necessary to change the number of nozzles, the distance between them, the spraying width, and the speed. In each case, the required calculations are performed.

Aeroplanes and helicopters outfitted with special equipment are employed for aerial spraying. The rates of use of a liquid in aerial

spraying are 25, 50, 100, 150, and 200 litre/ha and are calculated by the formula:

$$Q = \frac{10\,000q}{vw}$$

where Q = rate of use of the liquid, litre/ha
q = rate of flow (discharge) of the liquid from the aerial sprayer, litre/s
v = speed of the aircraft, m/s
w = spraying width, m.

This formula is also used to calculate the rate of flow of the liquid per second (q) for the preset rate of use (Q). It is checked at the aerodrome, and the equipment is adjusted if necessary. The correctness of the established rate of use of the liquid is also checked after the first flights by measuring the treated area.

Concentration of Working Solution. The concentration of the solution changes depending on the rate of use of the solvent liquid, which is associated with the employment of ground or aerial equipment, and is calculated by the formula:

$$c = \frac{100R}{Q}$$

where c = concentration of the working solution, %
R = rate of use of the herbicide (formulation), kg/ha
Q = rate of use of the liquid, litre/ha.

For example, in the aerial spraying of a 40% amine salt of 2,4-D with a rate of use of the formulation of 2.5 kg/ha and of the solvent of 25 litre/ha, the concentration of the working solution will be $(100 \times 2.5)/25 = 10\%$, while when sprayed by a tractor sprayer at a rate of 250 litre/ha, it will drop to one-tenth of this value and be $(100 \times 2.5)/25 = 10\%$. In spraying, it is essential to strictly control the rate of use of the liquid per unit area. An arbitrary increase or decrease in the rate of use of the liquid during work will lead to a decrease or increase in the rate of application of the herbicide, which cannot be tolerated.

8.4. Contact Herbicides

8.4.1. Petroleum Oils

The products of petroleum refining consist of a mixture of various saturated, unsaturated, and aromatic hydrocarbons.

The phytotoxicity of petroleum (mineral) oils is due to their containing aromatic and unsaturated hydrocarbons and depends on the boiling point and the viscosity. Oils with a low boiling point (for example, petrol), although phytotoxic, rapidly evaporate because of their high volatility and do not exhibit a toxic effect. Oils with

a high boiling point and a greater viscosity penetrate poorly into plants and also function poorly as herbicides.

Petroleum diesel fuel belongs to the non-selective herbicides.

To increase the herbicidal action of mineral oils, DNOC is added to them. In this case, the oils are said to be fortified. They are used as non-selective herbicides.

Mineral oils wet identically well both sensitive plants and plants resistant to them, and penetrate into the plant tissues via the stoma and cuticle. In sensitive plants, however, oils penetrate into both the intercellular spaces and the cells; the plasma membrane dissolves in the oil, and the cells perish.

In resistant plants such as carrots, the cell walls are thicker and are hydrated, while the cell membrane is impervious to mineral oils. It is also presumed that aromatic hydrocarbons penetrate into the cells of plants that are sensitive and resistant to mineral oils, but in the cells of the resistant plants they are rendered harmless as a result of oxidation of the toxic hydrocarbons, and the oxidation products are included into the general course of metabolism. It has been noted that in plants resistant to mineral oils their respiratory energy substantially grows after treatment, which points to a more intensive oxidation process.

8.4.2. Phenol Derivatives

Phenols are distinguished by their high physiological activity and are universal pesticides. Their pesticidal activity grows when a nitro-group, a halogen, or an alkyl is introduced into the aromatic radical. Phenols and their derivatives are phytocidal, they burn plants and act like contact herbicides. Nitrogen and halogen derivatives of phenol are used as herbicides. Phenol derivatives have an acute toxicity to humans and warm-blooded animals. Phenols exhibit a toxic action with respect to plants in different ways. At low concentrations, they inhibit the process of phosphorylation, and break the chains of the reactions forming the phosphates adenasine di- and triphosphate rich in energy; when the concentration of phenols in a plant increases, they inhibit respiration and precipitate proteins (denaturation).

The selectivity of action of phenols is due to the physiological and biochemical features of plants.

DNOC

The active ingredient is 2-methyl-4,6-dinitrophenol. The sodium salt of DNOC is used as a contact herbicide.

The sodium salt of DNOC is marketed in the form of a yellow powder containing 40% of the active ingredient and well soluble in water.

Ammonium sulphate is added to the sodium salt as an activator to improve its penetration into a plant and intensify its action.

DNOC kills weeds such as common spurrey, hempnettle, cleavers, and black nightshade that are resistant to 2,4-D.

It is used for killing vegetating weeds on fields of perennial cereal grasses by preemergence and postemergence spraying at a rate of 3-5 kg of the formulation (1.2-2 kg a.i.) per hectare; on seed fields of perennial cereal grasses by spraying in the first year of vegetation, beginning from the tillering stage, at a rate of 10-12 kg of the formulation (4-4.8 kg a.i.) per hectare. It is prohibited to feed the green matter to cattle.

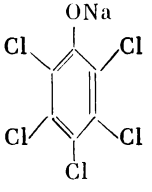
DNOC is used against dodder on clover and alfalfa fields, for which purpose the infected sections in two or three days after hay cutting are sprayed with a herbicide solution at a rate of 35-50 kg of the formulation (14-20 kg a.i.) per hectare with the liquid used at a rate of 500 litre/ha.

The dodder is killed, while the perennial grasses grow again.

DNOC is highly toxic to humans and warm-blooded animals (LD_{50} for rats is 40-65 mg/kg).

No residues of DNOC in food products are tolerated.

Sodium Pentachlorophenolate (Santobrite)



The formulation used as a herbicide is a powder containing 92% of the active ingredient, well soluble in water. It is effective for killing dodder on clover and alfalfa fields by treating the seats in three days after hay cutting, spraying them at a rate of 15-25 kg of the formulation (14-23 kg a.i.) per hectare.

Sodium pentachlorophenolate is recommended for pilot application on corn, soybean, and potato fields by preemergence spraying at a rate of 15-25 kg of the formulation (14-23 kg a.i.) per hectare.

The formulation can be used for killing weeds on areas with no cultivated crops.

It is toxic to humans and warm-blooded animals (LD_{50} for rats is from 36 to 210 mg/kg). No residues are tolerated in food products.

Nitrafen

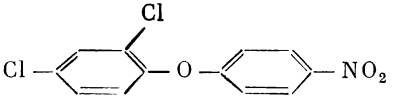
Nitrafen includes the products of nitration of the alkylphenols separated in the processing of shale or coal that contain 30-35% of water. It is marketed in the form of a thick paste soluble in water. It is a good killer of wild radish, fat hen, hempnettle, charlock, and amaranth in the phase of two or three leaves.

It is recommended for killing dodders on clover and alfalfa fields by spraying the stubble not later than in two or three days after hay cutting at a rate of 40-75 kg (24-45 kg a.i.) per hectare.

It is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 900-1300 mg/kg).

Nitrofen (Nitrochlor, TOK, NIP)

The active ingredient is 2,4-dichloro-4-nitrophenyl ether:



It is a light cream-coloured solid melting at 70-71 °C, poorly soluble in water (0.7-1.2 mg/litre at 22 °C), and soluble in acetone, dioxane, ethanol, and benzene.

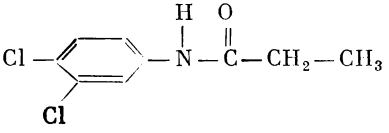
Nitrofen is marketed in the form of a 25% emulsifiable concentrate and is recommended for pilot application on plantations of clary sage of the first year of vegetation by spraying the crop in the stage of two true leaves and a leaf rosette.

The rate of use of the formulation is 16 kg (4 kg a.i.) per hectare. It has a low toxicity to warm-blooded animals (LD_{50} for rats is 7850 mg/ha).

8.4.3. Amides and Nitriles of Aliphatic Carboxylic Acids

Propanil (Stam F-34, Surcopur)

The active ingredient is 3,4-dichlorophenylpropionanilide:



It is a white crystalline solid melting at 92-93 °C. Its solubility in water is about 225 mg/litre; it dissolves well in ketones, aromatic hydrocarbons, and their halogen derivatives.

The main product of transformation of propanil in the soil is tetrachlorazobenzene, which is also detected in plants after the hydrolysis of propanil by the formation of 3,4-dichloroaniline.

The technical formulation is a solid poorly soluble in water and well in organic solvents.

It is marketed in the form of an emulsifiable concentrate containing 30% of the active ingredient and of a 50% solution.

Propanil is used for killing millet-like dicotyledonous weeds on paddy fields. The rice is sprayed with a propanil emulsion in the stage of 1-4 leaves; at this time the weeds have 1-2 leaves and are sensitive to this herbicide. To ensure the more complete killing of the weeds, the rice is sprayed with propanil after the water has been drained from the plots at a rate of the 30% formulation of 16.7-30 kg (5-9 kg a.i.) per hectare. Water is not fed onto the plots during one or two days. This way of applying propanil gives excellent results against the main weeds of rice: jungle rice, Japanese millet, and barnyard grass.

Propanil in the form of a 50% solution is recommended for application by ultrasmall-volume spraying at a rate of 6-10 kg of the formulation (3-5 kg a.i.) per hectare also in the stage of 1-4 leaves of the rice plants, in all rice-growing regions of the USSR except for the Uzbek SSR and the Far East.

Propanil is also recommended for killing weeds on coriander fields by spraying in the stage of two or three true leaves in the crop at a rate of 13.3-20 kg of the formulation (4-6 kg a.i.) per hectare.

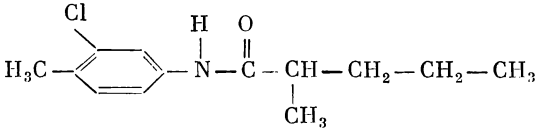
Propanil has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 1380 mg/kg). Its tolerance level in rice is 0.3 mg/kg.

It is prohibited to breed fish in flooded check plots treated with propanil. The possibility of contamination of fish-breeding ponds situated directly on a farm's lands must also be prevented.

After aerial treatment, propanil is detected in the flooded plot water of paddy fields and drain ditches in an amount of 0.3-0.5 mg/litre. It is not detected in the soil in a year after treatment.

Pentanochlor (Solan)

The active ingredient is 3′-chloro-4′-methyl-α-methylvaleranilide:



In the pure form, it is a white to pale cream powder poorly soluble in water (8-9 mg/litre at room temperature). Its solubility in xylene is 20-30%, and in diisobutyl ketone is 46%.

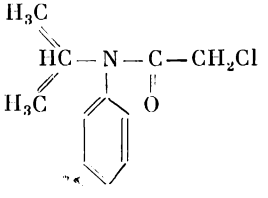
For practical use, it is marketed in the form of an emulsifiable concentrate containing 46.9% of the active ingredient.

Pentanochlor is a contact herbicide recommended for controlling weeds on tomato plantations. It is best used for postemergence killing of weeds on tomato plantations during two weeks after planting the seedlings by spraying at a rate of 8-10 kg of the formulation (3.75-4.7 kg a.i.) per hectare when the weeds are in the stage of one or two leaves. Pentanochlor persists in the soil from one to two months. It kills common spurrey, fat hen (pigweed), common chickweed, wild radish, hempnettle, etc. It has been established that in sensitive plants pentanochlor inhibits the Hill reaction, suppresses the absorption of CO_2, and, probably, inhibits the enzymes participating in respiration.

Pentanochlor has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 10 000 mg/kg). Its tolerance level in tomatoes is 1.5 mg/kg.

Propachlor ***(Ramrod, Bexton)***

The active ingredient is 2-chloro-N-isopropylacetanilide (also 2-chloro-N-isopropyl-N-phenylacetamide):



In the pure form, it is a light tan crystalline solid melting at 67-76 °C, slightly soluble in water (700 mg/litre), and soluble in organic solvents: 30.9% in acetone, 50% in benzene, 37.6% in chloroform, and 25.5% in toluene.

It is marketed in the form of a 65% wettable powder.

Propachlor is a preemergent herbicide very effective against many mono- and dicotyledonous weeds such as Japanese barnyard grass, bristle grass, common chickweed, amaranth, shepard's purse, and groundsel.

Wild radish, common spurrey, knotweed, fumitory, field pansy, etc. are more resistant to this herbicide.

Propachlor is recommended for the spraying of the weeds before emergence of the crop or before planting the seedlings of Jersey kale and white cabbage, and also before emergence of onions, garlic, swedes, and turnips at a rate of 7-10 kg of the formulation (4.6-6.5 kg a.i.) per hectare.

Propachlor persists in the soil up to 6-8 weeks.

It is moderately toxic to humans and warm-blooded animals (LD_{50} for mice and rabbits is 300-500, and for rats is 1056 mg/kg).

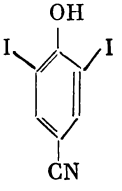
The tolerance level of propachlor in cabbage and other vegetables is 0.2 mg/kg.

8.4.4. Hydroxybenzoic Acid Derivatives

Actril AS

This is a combined formulation consisting of a mixture of ioxynil in an amount of 150 g/litre and MCPA in an amount of 240 g/litre. It is marketed in the form of a 32% aqueous solution.

The active ingredient of ioxynil is 4-hydroxy-3,5-di-iodobenzonitrile:



It is a colourless, odourless solid melting at 212-213.5 °C (with decomposition), virtually insoluble in water (50 mg/litre at room temperature) and poorly soluble in organic solvents.

To prepare combined formulations of actril M and actril AS, alkali metal salts of ioxynil in organic solvents are marketed.

Ioxynil is characterized by contact action, although its ability to move slightly in plants has been noted, which leads to chlorosis of the tissues. In tests with plants sensitive to ioxynil, in already one day after treatment necrotic spots appear on the leaves and shoots, and in 2-7 days the plants perish.

Gramineous plants are resistant to ioxynil, as are Canadian thistle, field sowthistle, and common horsetail. Plants with a wax coating have been noted to be more resistant to this herbicide. Many dicotyledonous weeds (scentless mayweed, knotweed, common chickweed, cleavers or pigtail, etc.) are sensitive to ioxynil.

The combined herbicides actril AS and actril M, which are prepared on the basis of ioxynil, MCPA, and mecoprop may be related to herbicides with both contact and systemic action.

It is good to use actril AS in cereal crops against biennial dicotyledonous weeds resistant to 2,4-D and MCPA such as common chickweed, fumitory, and common spurrey. Actril AS has only a slight effect on perennial offset and gramineous weeds, and also on field pansies.

It is recommended for killing weeds resistant to 2,4-D and MCPA on grain fields in the tillering stage at a rate of 1.2-3 kg of the formulation (0.4-0.95 kg a.i.) per hectare.

Actril M

This is a combined formulation consisting of a mixture of two herbicides: ioxynil in an amount of 150 g/litre and mecoprop in an amount of 375 g/litre. It is marketed in the form of an aqueous 52% solution.

In tests, actril M showed a high effectiveness against dicotyledonous annual and biennial weeds such as scentless mayweed, common spurrey, common chickweed, fumitory, and field pennycress.

This herbicide has a weak effect against gramineous weeds, perennial offset weeds, and also field pansies.

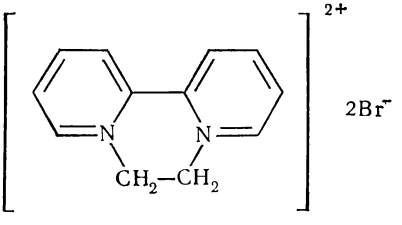
It does not harm spring and winter wheat and barley.

It is recommended for killing weeds resistant to 2,4-D and MCPA on wheat, barley, rye, and oat fields by spraying in the tillering phase at a rate of 1-3.5 kg of the formulation (0.5-1.8 kg a.i.) per hectare. Actril AS and actril M are formulations with a moderate toxicity (LD_{50} for rats is 753-850 mg/kg).

8.4.5. Heterocyclic Compounds

Diquat (Reglon, Aquacide)

The active ingredient is 1,1′-ethylene-2,2′-bipyridylium dibromide:



It is a white crystalline substance melting at 335-340 °C and well soluble in water (700 mg/litre at 20 °C).

It is marketed in the form of a 20% aqueous solution of the dibromide. The cation is the biologically active part of the molecule. Aqueous solutions are not volatile, are stable in an acid or neutral medium, while under the action of strong alkalies they form coloured complex products.

Concentrated solutions corrode metals such as steel, sheet metal, and galvanized tin plate, therefore diquat must be stored in polyethylene carboys.

Diquat is a non-selective contact herbicide. It is characterized by a rapid herbicidal effect and kills the green part of plants even in small doses. It is also used as a defoliant and desiccant.

Diquat is not absorbed by old bark, therefore it can be used to spray the circular areas around the trunks of fruit trees. In definite conditions in the light and at a high relative humidity (100%), diquat can move along the xylem, which accelerates the death of the green part of plants.

Diquat rapidly decomposes on the surface of the soil under the influence of ultraviolet rays, and in the soil by the activity of microorganisms. Certain yeasts, and also the anaerobic bacterium *Clostridium pasterianum* are capable of decomposing diquat. This explains why residual amounts of the herbicide do not accumulate in the soil.

Diquat kills many dicotyledonous weeds, including the Canadian thistle, and can be used for the chemical treatment of fallow fields, for improving meadows and pastures with a poor grass stand (diquat kills the weedy grass stand, after which fodder grasses are planted), and for killing weeds before planting cultivated plants, or after planting, but before their emergence.

The mechanism of action of diquat on plants has not been revealed completely. It has been established that dipyridyls (diquat, paraquat) inhibit the transfer of electrons in photosynthesis. The iron-containing protein ferredoxin is known to be the carrier of electrons in plants. It is therefore presumed that dipyridyls may replace ferredoxin in photosynthesis reactions, which may disrupt the process and kill the plant owing to insufficient nutrition and the loss of energy. The assumption was also advanced that secondary oxidation of dipyridyls by molecular oxygen results in the accumulation of reactive hydroperoxide radicals, which are just what destroys the plant cells.

Diquat is recommended for killing weeds on fallow fields in regions subjected to wind erosion. In this case, it is applied by spraying the vegetating weeds two or three times during a season at a rate of 5-10 kg of the formulation (1-2 kg a.i.) per hectare. It is also recommended for improving the composition of the grass stand on hay-growing fields and pastures, and for killing weedy and poisonous motley grass—false hellebore, buttercup, dock, marsh marigold, etc. by spraying the vegetating weeds in the spring at a rate of 10-15 kg of the formulation (2-3 kg a.i.) per hectare. Clusters of harmful and poisonous weeds may be sprayed in the period of vegetation at a rate of 10 kg (2 kg a.i.) per hectare.

Diquat is a moderately toxic substance (LD_{50} for rats is 400 mg/kg). The tolerance level of diquat in food products is 0.05 mg/kg.

8.4.6. Inorganic Herbicides

Calcium ***Cyanamide (Cyanamide, Nitrolime)***

This substance is a dark-gray, almost black dusty powder with an odour of acetylene poorly soluble in water. It decomposes in the soil to form hydrogen cyanamide, urea, ammonia, nitrates and nitrites. Weeds are killed by the nitrites and hydrogen cyanamide. It is applied as a selective herbicide by dusting before planting, before emergence of the crop, and upon emergence of some crops. It kills many dicotyledonous weeds such as fat hen, common chickweed, charlock, and Shepard's purse, especially at a young age. It is recommended to apply calcium cyanamide onto common onions and onion sets before emergence and over the shoots at a height of the onions of 6-8 cm at a rate of 260-350 kg (49.4-66.4 kg a.i.) per hectare.

The action of calcium cyanamide on weeds is intensified when dusting plants moistened by dew or rain. Calcium cyanamide is moderately toxic to humans and warm-blooded animals (LD_{50} for mice is 400 mg/kg).

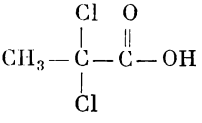
It is prohibited to use the tops of onions from treated plots in food.

8.5. Systemic Herbicides

8.5.1. Aliphatic Carboxylic Acid Derivatives

Dalapon (Basfapon, Ded-Weed, Dowpon)

The active ingredient is 2,2-dichloropropionoic acid:



It is a liquid boiling at 185-190 °C, well soluble in water and alcohol. It forms salts, among which the sodium salt (CH_3CCl_2COONa) is used as a herbicide. Sodium 2,2-dichloropropionate is a white hygroscopic powder decomposing at 166.5 °C and well soluble in water (502 g/litre at 25 °C). The technical product contains 85% of the active ingredient.

Dalapon hydrolyzes in an aqueous solution, at an increasing rate with elevation of the temperature. This is attended by the formation of pyrovinic acid non-toxic to plants, hence a working solution of dalapon must be prepared directly before application.

Dalapon is absorbed by leaves and roots, therefore it may be used both before and after emergence of the weeds. Since the substance rapidly decomposes in the soil, it is better to apply it over the shoots of weeds.

Dalapon kills gramineous weeds: annual ones such as green bristle grass, yellow foxtail grass, barnyard grass, wild oats, and perennial ones such as couch grass, Aleppo grass, and blue couch grass. The herbicide moves in young plants along the phloem both into the roots and into the leaves, but accumulates in the meristemic tissues.

The action of dalapon in plants is associated with disruption of the synthesis of the pantothenic acid contained in the coenzyme A, one of the enzymes responsible for the translocation of the acetyl groups in the metabolism of carbohydrates, fats, and nitrogen. Dalapon disrupts the synthesis of auxins, inhibits the synthesis of pyrovinic acid, and denatures proteins. It has been noted that dalapon hinders the formation of the wax coating of leaves. Such diverse disruptions of the biochemical processes in plants lead to their perishing. The reasons why dalapon acts only on gramineous weeds have not been studied adequately to date.

In gramineous plants harmed by dalapon, the leaves curl, bend, and abundant tillering is observed. But dalapon acts slowly, even plants sensitive to it perish in two or three weeks after treatment. Dalapon is more toxic to young rapidly growing plants with good moistening.

Since dalapon accumulates in the meristems of stalks and leaves, it is not recommended for application to plants intended as food for humans and as fodder for livestock in the green form.

Dalapon is recommended for killing gramineous weeds in orchards at least three years old, on berry plantations and on grapevines by directed spraying (not over two treatments a season). It is necessary to prevent the solution from getting onto the crops. The rate of use of dalapon is 4.7-10 kg (4-8.5 kg a.i.) per hectare.

Dalapon is also used to kill weeds in land reclamation systems and along open canals of collecting and draining networks by spraying vegetating weeds at a rate of 10-20 kg of the formulation (8.5-17 kg a.i.) per hectare. The use of dalapon in the autumn at the same rates is effective when preparing fields for flax, potatoes, beets, for planting currants, gooseberries, raspberries, and tea shrubs. In this case, dalapon is sprayed at the end of the summer or in the autumn.

Dalapon is also used after fall ploughing on cotton fields to kill blue couch grass by spraying at a rate of 40-55 kg of the formulation (34-47 kg a.i.) per hectare.

Dalapon has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 6600-8100 mg/kg). The tolerance level in fruits and grapes is 1 mg/kg.

TCA (Sodium-TCA)

The active ingredient, trichloroacetic acid (CCl_3COOH), is a white crystalline substance well soluble in water, alcohol, and ether. Among the salts of this acid, the greatest favour as a herbicide has been given to sodium trichloroacetate (CCl_3COONa)—a hygroscopic white to light brown crystalline solid well soluble in water. TCA contains 90% of the active ingredient. It relates to selective herbicides with root action used to kill gramineous plants, both annual and perennial ones, such as bristle grass, barnyard grass, and couch grass.

The herbicide penetrates into a plant through its roots and moves into the stems, leaves, and points of growth along the xylem with the transpiration stream. In plants sensitive to TCA, it causes changes in form: curling of the leaves and stems, disruption of the growth of individual organs, and stopping of the formation of wax on the leaves. TCA disrupts the processes of respiration and photosynthesis in plants, the supply of nutrient substances, increases the content of amino acids, and disarranges nitrogen metabolism. It inhibits the synthesis of pantothenic acid from pantoic acid and β-alanine; in addition, under the action of this herbicide in sensitive plants, oxidation and phosphorylation in the respiratory chain are separated, the enzyme systems and the structure of the mitochondria itself are disrupted.

TCA decomposes in the soil in 1.5-3 months even when incorporated in large doses. This process occurs more rapidly in fertile, well moistened soils with a high activity of the microorganisms.

Cabbage, carrots, celery, tomatoes, beets, flax, peas, and vetch are resistant to TCA; pumpkins, cotton, potatoes, onions, and alfalfa are less resistant; clover, lupine, beans, and cereals are sensitive to it.

To control gramineous weeds, TCA is used both in the spring before planting of the crops, and in the autumn in the system of fall ploughing. It is recommended for application in the spring on fields intended for onions, peas, carrots, sugar, fodder, and table beets by preplanting spraying at a rate of 5-14 kg of the formulation (4.4-12.2 kg a.i.) per hectare.

In pip fruit orchards (at least four years old), TCA is incorporated in the early spring when cultivating the soil at a rate of 15-20 kg (13-17.4 kg a.i.) per hectare. In the autumn, the rate is increased to 29-40 kg (25.8-34.8 kg a.i.) per hectare. Autumn spraying of TCA at the same rate is used to prepare fields for the planting of berries—currants and gooseberries. The autumn treatment with TCA is recommended on lands contaminated with wheat grass when preparing the soil for potatoes, carrots, and cucumbers at a rate of 23-50 kg of the formulation (20-43.5 kg a.i.) per hectare. When preparing fields for cotton, to eradicate blue couch grass, it is recommended to

incorporate TCA after fall ploughing at a rate of 100-120 kg of the formulation (87-104 kg a.i.) per hectare.

When applied in the autumn, TCA decomposes completely by the time of planting of the crops in the spring, and its residues are not detected in the soil.

TCA may be used on fields growing the Caucasian yam drug plant before emergence and growth of the crop at a rate of 17 kg (14.8 kg a.i.) per hectare.

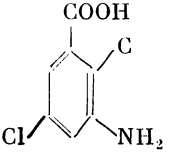
TCA has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 3300 mg/kg). The tolerance level for vegetables, fruits, and grain is 0.01 mg/kg.

8.5.2. Benzoic Acid Derivatives

Among benzoic acid derivatives, choramben, dicamba, 2,3,6-TBA, and chlorthiamid have found widespread application.

Chloramben (Amiben, Vegiben)

The active ingredient is 3-amino-2,5-dichlorobenzoic acid:



In the pure form, it is a white odourless solid melting at 200-201 °C. Its solubility in water is 700 mg/litre at 20 °C. It is stable to oxidation and heating.

Chloramben is marketed in the form of a 25% emulsifiable concentrate. It is a systemic herbicide. Both the leaves and the roots absorb it well. The roots of resistant plants such as soybeans also absorb chloramben, but only an insignificant part of it is translocated into the green parts.

In plants, chloramben combines with the components of the cells. One of the metabolites is N-glucosylchloramben.

Chloramben kills many mono- and dicotyledonous weeds both in preemergent incorporation into the soil and in postemergent spraying of them.

The weeds sensitive to chloramben include wild oats, bristle grass, amaranth, common chickweed, knotgrass, and fat hen.

In the preemergence incorporation of chloramben, soybeans, tomatoes, potatoes, and cotton are resistant to it.

Chloramben decomposes in the soil under the action of ultraviolet radiation and microorganisms. It is absorbed mainly by the organic

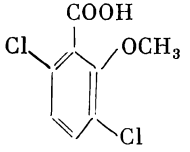
matter and clay particles of the soil, consequently in heavy loams chloramben does not migrate into the deeper layers of the soil. This occurs in light soils.

Chloramben is recommended for pilot use on tomato plots by spraying the soil before planting of the seedlings and on soybean plots before emergence of the crop at a rate of 16-24 kg of the formulation (4-6 kg a.i.) per hectare.

Chloramben has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 4200, and for mice is 2400 mg/kg). The tolerance level for tomatoes and cabbage is 0.25 mg/kg.

Dicamba (Banvel, Dianat)

The active ingredient is 2-methoxy-3,6-dichlorobenzoic acid (or 3,6-dichloro-*o*-anisic acid):



In the pure form, it is a white crystalline solid melting at 114-116 °C. It dissolves poorly in water (4.5 g/litre at 25 °C) and well in organic solvents. Salts of alkali metals and amines dissolve well in water. At room temperature, the solubility of the dimethylamine salt is 720 g/litre.

Dicamba is marketed in the form of a 48% aqueous solution of its dimethylamine salt.

The herbicide penetrates well into plants through their leaves and roots and is translocated along the vascular system both via the phloem and via the xylem.

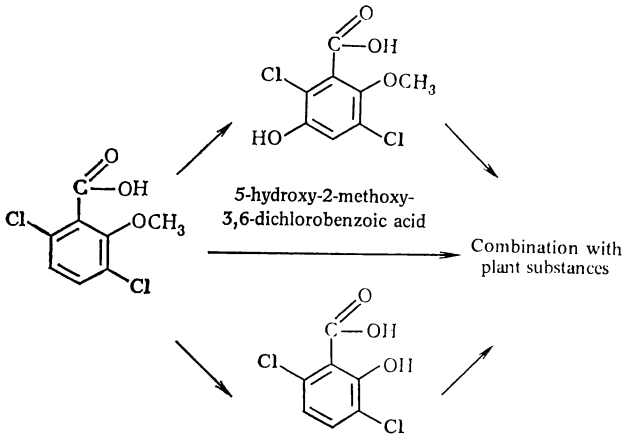
The time needed for the complete decomposition of dicamba in plants when applied in the recommended doses is considerably shorter than the period from planting to ripening of cereal crops, therefore no residues of the herbicide are detected in them by the time of harvesting.

In sensitive plants, dicamba accumulates in the young growing leaves, decomposes slowly, and exhibits its toxic effect.

In the soil, dicamba migrates downward and upward following the movement of the soil's moisture, and microorganisms decompose it quite slowly. The herbicide is absorbed better in soils rich in organic matter.

In gramineous plants most resistant to this herbicide, dicamba is uniformly distributed over the entire plant and decomposes quite rapidly. A considerable portion of the dicamba may be excreted into the surroundings from the root system. Dicamba decomposes in plants resistant to it (wheat, meadow grass) according

to the following scheme (after P. Kearney and D. Kaufman, 1969):



Cereal crops in the tillering stage are resistant to dicamba. In comparatively small doses, this herbicide kills many dicotyledonous weeds resistant to 2,4-D and MCPA such as bushy knotweed, black bindweed, common chickweed, cleavers, (pigtail), charlock, and groundsel.

In larger doses, dicamba kills perennial weeds such as field bindweed, Canadian thistle, Russian knapweed, and perennial ragweed. These weeds may be treated with dicamba at the seats of their spreading, and also on meadows and pastures and on plots with no cultivated plants.

Dicamba is used to prepare combined herbicides (banlen, diamet-D, dialen, etc.) by mixing with MCPA and 2,4-D.

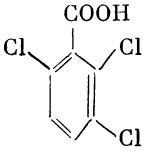
It is recommended to add dicamba to 2,4-D and MCPA (0.07-0.24 kg a.i./ha) in treating cereal crops.

Dicamba is recommended for pilot application against Russian knapweed and other perennial offset weeds by spraying their beds, and also on land not used for agricultural purposes at a rate of 6-40 kg of the formulation (2.9-19.2 kg a.i.) per hectare.

It is also recommended for killing weeds and poisonous motley grass on haymaking fields and pastures (false hellebore, buttercup, cow parsnip, dock, etc.) with summer spraying at a rate of 1.5-2 kg of the formulation (0.75-0.95 kg a.i.) per hectare and autumn spraying at a rate of 2.6-3.1 kg (1.25-1.5 kg a.i.) per hectare. Dicamba has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 1200-3000 mg/kg).

2,3,6-TBA (Polydim, Tribac)

The active ingredient is 2,3,6-trichlorobenzoic acid:



In the pure state, it forms white to buff hard crystals melting at 87-89 °C, poorly soluble in water (7.7 g/litre at 22 °C) and readily soluble in most organic solvents. The sodium, potassium, and amine salts of 2,3,6-trichlorobenzoic acid dissolve well in water. The formulation contains 15.7% of the dimethylamine salt of 2,3,6-trichlorobenzoic acid and 10.4% of other isomers—2,3,4-, 2,3,5-, 2,4,6-, and 3,4,5-trichlorobenzoic acids.

2,3,6-TBA penetrates into plants through their leaves and roots and is readily translocated in them. It induces reactions in plants that are typical for herbicides of the type of synthetic growth regulators, is distinguished by a prolonged persistence, and is slowly inactivated in plants and in the soil. When mixed with MCPA, formulations of 2,3,6-TBA play the role of synergists and intensify the action of the mixture.

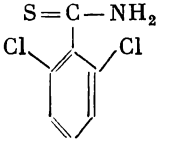
2,3,6-TBA is marketed in the form of a 45% water-soluble concentrate and is recommended for eradicating seats of Russian knapweed by spraying the vegetating plants in their beds in the stage of rosette and beginning of stem growth at a rate of 70-120 kg of the formulation (31.5-54 kg a.i.) per hectare.

Drifting vapour and drops of 2,3,6-TBA may damage crops such as beans, tomatoes, cotton, and tobacco.

2,3,6-TBA is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 750 mg/kg). It must be noted that the organic solvent in the formulation may cause irritation of the mucous membranes.

Chlorthiamid (Prefix)

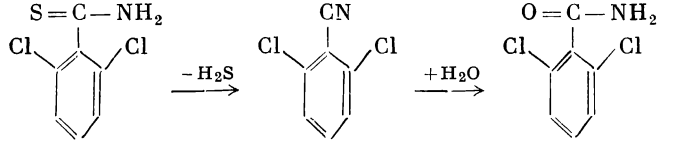
The active ingredient is 2,6-dichlorothiobenzamide:



In the pure form, it is a white crystalline solid melting at 151-152 °C and sparsely soluble in water (950 mg/litre at 21 °C). It dis-

solves well in aromatic and chlorinated hydrocarbons. Chlorthiamid is stable to the action of light and heating up to 90 °C. It hydrolyzes in an alkaline solution, and is more stable in an acid one.

It is prepared for practical use in the form of a 75% wettable powder. When incorporated into the soil, the herbicidal activity of chlorthiamid persists up to 4-6 months. This is the result of the formation of a metabolite with a high herbicidal activity, namely, cyano-2,6-dichlorobenzoic acid (dichlorocyanobenzene). This is a microbiological process. In the first step, hydrogen disulphide is detached and dichlorocyanobenzene is formed, and then water is attached, and a compound having a low activity is formed—the amide of 2,6-dichlorobenzoic acid:



Chlorthiamid — Dichloro-cyanobenzene — Amide of 2,6-dichlorobenzoic acid

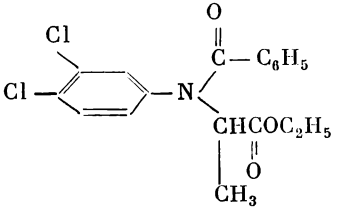
The plants absorb both chlorthiamid and its metabolites with their roots and underground shoots, and these substances migrate into the green organs.

Chlorthiamid migrates poorly in the soil and remains in the top 10-centimetre layer, which allows it to be used in fruit growing. It is recommended for pilot use in pip and stone fruit orchards (apples, pears, plums, cherries, apricots, peaches) by spraying the soil before the emergence of the weeds in a dose of 5-10.6 kg of the formulation (3.8-8 kg a.i.) per hectare. Here it is necessary to prevent the working liquid from getting onto cultivated plants. When applied in this way, chlorthiamid kills many mono- and dicotyledonous annual and biennial weeds.

The substance is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 757 mg/kg, for mice is 500 mg/kg, and for rabbits is 300 mg/kg).

Benzoylprop Ethyl (Suffix)

The active ingredient is ethyl N-benzoyl-N-(3,4-dichlorophenyl)-2-aminopropionate:



It is an off-white crystalline powder melting at 70-71 °C. It is poorly soluble in water (about 20 mg/litre at 25 °C) and soluble in methanol, acetone, and carbon tetrachloride.

For practical application, benzoylprop ethyl is marketed in the form of an emulsifiable concentrate containing 20% of the active ingredient. It is recommended for pilot application against wild oats on spring wheat fields by spraying the seedlings of the crop, beginning from the stage of two or three leaves before the stem extension stage at a rate of 5-7.5 kg (1-1.5 kg a.i.) per hectare. Benzoylprop ethyl has a moderate and low toxicity to humans and warm-blooded animals (LD_{50} for rats is 1555 mg, and for mice is 716 mg/kg).

8.5.3. Arylhydroxyalkylcarboxylic Acids

This group of herbicides includes derivatives of arylhydroxyacetic acids (2,4-D and MCPA), arylhydroxypropionic acids (mecoprop), and of arylhydroxy-γ-butyric acids (MCPB and 2,4-DB).

Derivatives of phenoxyacetic acids have been given the greatest preference at present.

1. Phenoxyacetic Acid Derivatives

Among the various derivatives of phenoxyacetic acids, 2,4-D (salts and esters) and MCPA (salts) are widely used as herbicides.

The chemical properties of these herbicides are due to the aromatic radical (phenyl) and the presence of the carboxyl group COOH. We can consider 2,4-D (2,4-dichlorophenoxyacetic acid) as a derivative of 2,4-dichlorophenol into whose hydroxyl group an acetic acid residue has been introduced.

These compounds form salts with inorganic and organic bases that are sufficiently stable in the solid and liquid state. With alcohols, they form esters that are widely used as herbicides.

The physiological activity of phenoxyacetic acid increases when a halogen such as fluorine or chlorine is introduced into the aromatic radical, the position of the halogen being very important. For example, in the dichlorophenoxyacetic acid series, 2,4-dichlorophenoxyacetic acid has the highest physiological activity, and 2,6-dichlorophenoxyacetic acid has the lowest activity. The latter decreases depending on the chlorine atom positions as follows: 2,4-D > 2,5 > 3.4 > > 3,5 > 2,6.

When one hydrogen atom is substituted by an aliphatic hydrocarbon radical in a molecule of a phenoxyacetic acid, the activity of the compound grows insignificantly.

Esters of phenoxyacetic acids have a more pronounced herbicidal activity, which is explained by their better ability of penetrating

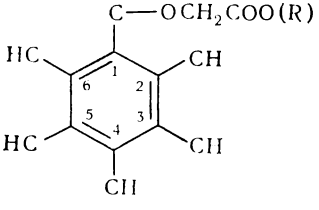
through the epidermal tissues of plants, and first of all through the cuticle.

The salts of phenoxyacetic acids with organic bases are also more phytocidal than those with alkali metals. For example, the herbicidal activity of the triethanolamine salt of 2,4-D is considerably higher than that of the sodium salt.

Table 24. Structure of Herbicides—Derivatives of Phenoxyacetic Acids

Formulation	Substitutes		
	of hydrogen in aromatic radical		R
	position	substitute	
2,4-D (2,4-dichlorophenoxyacetic acid)	2,4	Cl	H
Sodium salt of 2,4-D	2,4	Cl	Na
Triethanolamine salt of 2,4-D	2,4	Cl	$H\ \ CH_2CH_2OH$ $\vert\ \ /$ $N{-}{-}CH_2CH_2OH$ $\backslash$ CH_2CH_2OH
Butyl ester of 2,4-D	2,4	Cl	$-C_4H_9$
Octyl ester of 2,4-D	2,4	Cl	$-C_8H_{17}$
MCPA (4-chloro-2-methylphenoxy-acetic acid	2—	CH_3	
MCPA	4—	Cl	Na, K

The general structure of herbicides that are derivatives of phenoxyacetic acids can be represented by the diagram (see also Table 24):



These herbicides penetrate well into plants through their leaves and roots, but are used more frequently for spraying vegetating plants with aqueous solutions and emulsions. The spraying periods are established depending on the phase of stability of the cultivated plants, the sensitivity of the weeds, and the weather.

When sprayed, the herbicides 2,4-D and MCPA get onto the leaves and stems in the form of minute drops, and to exhibit phytotoxic

activity they must penetrate into the leaves, surmounting the barrier formed by the protective tissues.

The herbicides may penetrate through the stomas, and also through the cuticle, which is permeable to hydrophilic and lipophilic compounds because it has micropores—ectodesmae.

Oil solutions of the herbicides penetrate better through the cuticle because they have a dissolving ability.

Aqueous solutions of the herbicides penetrate better through the cuticle when the plants are well moistened and the micropores of the cuticle are filled with water.

The cell walls are not an obstacle for herbicides—both lipophilic and hydrophilic substances penetrate well through them.

The herbicides penetrate better into young leaves with thinner epidermal tissues and open stomas in favourable weather conditions.

Numerous investigations have shown that undissociated 2,4-dichlorophenoxyacetic acid and its esters penetrate into the leaves of plants more rapidly than ions of 2,4-D from aqueous solutions of its salts. The permeability of 2,4-D can be intensified by acidifying its solution (pH 3-5) and adding the ions NH_4^+ and PO_4^- to the solutions.

Plants can also absorb vapours of aliphatic esters of 2,4-D. The esters of 2,4-D after penetrating into the leaves are rapidly hydrolyzed to 2,4-dichlorophenoxyacetic acid, and the latter is translocated along the vascular system.

Upon entering from the soil solution, 2,4-D migrates acropetally along the vessels of the xylem together with the stream of water and nutrient substances and may pass into the vessels of the phloem and back.

Upon getting into the mesophyll of a leaf, the herbicides are included into the common conveying system—the symplast, which consists of the cytoplasm of the cells joined by plasmodesma. The further translocation of 2,4-D is similar to that of the assimilation products, particularly saccharose, with the correction that the products of photosynthesis move along the symplast more rapidly than 2,4-D.

In experiments with beans treated with 2,4-D containing tracer atoms (Cenny and Markus, 1960), the herbicide was detected in the roots in 24 hours, while saccharose reached the roots already in 6 hours.

Saccharose is assumed to be the source of energy needed for the translocation of 2,4-D in plants.

The participation of macroergic compounds such as ATP (adenosine triphosphate) and ADP (adenosine diphosphate) points to the metabolic nature of translocation of 2,4-D in plants. It migrates along the symplast and vessels of the phloem forming complex com-

pounds with glucose and asparagic acid, which upon hydrolysis are capable of detaching free 2,4-D.

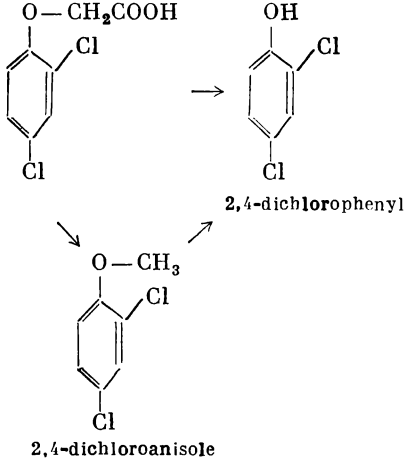
Retarding of the speed of translocation of 2,4-D in plants may be associated with damage to the phloem vessels, and also with absorption of the herbicide by the vegetative tissues and inclusion in the processes of metabolism.

Herbicides undergo transformations in plants that may lead either to intensification of their toxicity or to complete inactivation. Derivatives of 2,4-D undergo processes of metabolism in three directions: decarboxylation (destruction of the side chain and formation of CO_2 at its expense), hydroxylation (the introduction of a hydroxy group in the ring), and the formation of complex compounds with the metabolites.

The decomposition of 2,4-D in plants is associated with the different sensitivity or resistance of the plants to the herbicide. In many plants when 2,4-D enters them, rapid evolution of CO_2 occurs at the expense of decarboxylation. This path is characteristic of numerous plants such as northern red currants, lilac, and some varieties of apple trees.

The process of decarboxylation may occur by the complete breaking away of the side chain ($—CH_2COOH$), i.e. by breaking of the ether bond, or in steps, when the carbon dioxide in the carboxyl group first separates. Here an intermediate with one carbon atom in the side chain may be formed.

The decarboxylation of 2,4-D leads in the long run to the formation of 2,4-dichlorophenol:



2,4-D may lose its phytotoxicity in plants because of a reaction of hydroxylation, i.e. the introduction into the ring of the hydroxy

group —OH with the formation of 2,5-dichloro-4-hydrophenoxyacetic acid.

The formation of complex compounds of 2,4-D with the products of metabolism in plants also leads to the loss of phytotoxicity of this herbicide.

D. Chkanikov and his collaborators showed (1971) that in bean plants in 48 hours after introduction, 40% of the 2,4-D was in the form of water soluble glycosides of this acid. In wheat, peas, northern red and European black currants, a complex compound of 2,4-D with asparagic acid was detected.

V. Zemskaya and her collaborators discovered (1971) that in gramineous plants complex compounds of 2,4-D with the proteins of the vegetative cells are formed. This gave them the grounds to consider that the formation of such compounds is one of the reasons why these plants are resistant to 2,4-D.

The processes of decomposition of 2,4-D in plants occur quite rapidly, and its residues, as a rule, are not detected in the products. But sometimes, especially when the established regulations for applying this herbicide are not observed, its residues are detected in the grain, straw, green grass, and other products, which may result in their being destroyed because no residues of 2,4-D are tolerated in food products in the USSR.

In the soil, herbicides that are derivatives of 2,4-D also experience involved transformations and decomposition. Salts of 2,4-D soluble in water may be washed out into the deeper soil layers and get into the ground water. Esters of 2,4-D evaporate from the surface of the soil.

2,4-D herbicides also undergo photochemical decomposition, but the latter occurs mainly under the influence of microorganisms. This process occurs more rapidly in soils with a high microbiological activity. At present, some microorganisms capable of decomposing 2,4-D have been separated. They are *Mycoplana*, *Rhizobium*, *Corynebacterium*, *Arthrobacter*, *Achromobacter*, *Flavobacterium*, and certain actinomyces.

According to the results of numerous analyses, 2,4-D decomposes in soils during one month.

2. Mechanism of Action of Phenoxyacetic Acid Derivatives

In sensitive plants, the action of herbicides that are phenoxyacetic acid derivatives manifests itself quite rapidly. Already in a few hours, growth is inhibited or completely stopped, the petioles and young shoots curl, and the entire plant bends abnormally. Thickenings are formed in the lower parts of plants from which adventitious

roots appear. The upper parts of roots thicken and decay, and young roots die off.

The thickenings and fasciation of the shoots, leaves, and roots are attended by an increased turgor. As a result, the shoots and roots burst, and the wounds are infected by bacteria and fungi. The generative organs are also deformed: an increase in the number, separation, and growing together of the flowers, stamens, and carpels is observed, deformed fruits containing no seeds, empty underdeveloped ears are formed, etc.

All these morphological changes are very diverse and depend on the specific features of the plants, their age, and the weather conditions.

All the morphological changes and deformities are a consequence of the deep disruptions of the physiological processes in the plants. In plants treated with herbicides, the intensity of respiration first grows, then the process of photosynthesis is inhibited as a result of decomposition of the chlorophyll and the stopping of its biosynthesis. Hydrolytic decomposition of starch, inulin, and proteins occurs, and the processes of synthesis stop. As a result, during the first period after treatment, the content of mobile forms of carbohydrates and sugars in plants grows, while the content of stored and constitutional forms of plastic substances diminishes. The entry of nitrogen, phosphorus, and potassium into a plant sharply decreases, and the synthesizing activity of the root system terminates. Water metabolism is disrupted, the state of turgor is lost, and the plant wilts.

The causes of such deep and irreversible disturbances of the physiological processes have not yet been revealed adequately to date.

It has been established at present that 2,4-D discontinues oxidizing phosphorylation by inhibiting the esterification of the phosphate, with disruption of the process of formation of compounds rich in energy (macroergs)—ADP and ATP, consequently the energy exchange in plants is disrupted. It has also been established that 2,4-D strongly affects the synthesis of RNA (ribonucleic acid). This allows us to presume that the herbicides first affect the nucleic acids, and then, through the latter, the biosynthesis of proteins.

Disruption of the biosynthesis of structural and enzyme proteins leads to disruption of the processes of metabolism, the result being complete disarrangement of many aspects of metabolism in a plant's organism.

2,4-D noticeably affects the photosynthesis processes, first of all the photolytic activity of chloroplasts and photosynthetic phosphorylation. Studies have shown that 2,4-D inhibits the process of oxidizing and photosynthetic phosphorylation.

It is also known that 2,4-D has a sharp negative effect on the synthesis and transformation of growth stimulants in plants.

When considering all the aspects of the negative action of 2,4-D

on plants, one cannot fail to note that this herbicide, as well as other ones similar to it, inhibits the enzymes of plants. This can be a partial explanation of such deep disruptions in plants.

The addition of a large number of foreign molecules, for example, of 2,4-D to the cytoplasmic system causes disruptions such that not one, but possibly all the enzyme systems lose their equilibrium, and this leads to the disruption of most processes.

Amine Salt of 2,4-D (Triethanolamine Salt of 2,4-D)

This is a white crystalline solid well soluble in water. The marketed herbicide is a dark brown liquid containing 40% of 2,4-dichlorophenoxyacetic acid dissolving well in water.

The amine salt of 2,4-D is used for killing dicotyledonous weeds on fields with cereal crops, corn, perennial cereal grasses, and also on hay lands and fields intended for the planting of spring cereal crops and on some drug plants.

Cereal crops: wheat, rye, barley, and oats are sprayed with an amine salt solution in the tillering stage at a rate of 1.5-2.5 kg (0.6-1 kg a.i.) per hectare.

The same procedure is followed for millet at a rate of 1.5-2 kg (0.6-0.8 kg a.i.) per hectare. Sorghum is treated with the same doses in the stage of 3-6 leaves, corn is sprayed with the amine salt of 2,4-D in the stage of 3-5 leaves at a rate of 1.5-2.5 kg (0.6-1 kg a.i.) per hectare.

On castor-bean plant fields, the amine salt is applied before the emergence of the seedlings at a rate of 2-2.5 kg of the formulation (0.8-1 kg a.i.) per hectare. Buckwheat is treated two or three days before emergence at a rate of 4 kg (1.6 kg a.i.) per hectare.

Timothy grass is sprayed in the stage of 2-3 leaves at a rate of 2-3 kg (0.8-1.2 kg a.i.) per hectare. Smooth brome grass and meadow foxtail are sprayed in the tillering stage at a rate of 1-2 kg (0.4-0.8 kg a.i.) per hectare, orchard-grass is treated at the beginning of the tillering stage (0.75-1 kg, or 0.3-0.4 kg a.i. per hectare). Tall ryegrass and English blue-grass are first treated in the stage of 2-4 leaves at a rate of 0.75-1 kg (0.3-0.4 kg a.i.) while in the tillering stage the rate is increased to 2-3 kg (0.8-1.2 kg a.i.) per hectare. The treatment of perennial grasses with the amine salt of 2,4-D must be terminated 45 days before harvesting them.

On hay lands and pastures, the amine salt is employed for killing harmful and poisonous plants at a rate of 4-12 kg (1.6-4.8 kg a.i.) per hectare. The grazing of cattle and the mowing of the grass is permitted not earlier than 45 days after treatment. It is prohibited to treat areas closer than 200 m to water basins.

On fields to be used the following year for spring crops, the postharvest spraying of the amine salt of 2,4-D at a rate of 5-7.5 kg

(2-3 kg a.i.) per hectare makes it possible to kill perennial, biennial, and annual dicotyledonous weeds. Fallow fields in regions subjected to wind erosion are treated with the amine salt over vegetating weeds at a rate of 4 kg (1.6 kg a.i.) per hectare. This herbicide may be applied to plantations of common valerian of the first and second year of vegetation by spraying in 3-5 days after sowing or in the early spring (before growth of the crop) at a rate of 1.5 kg (0.6 kg a.i.) per hectare. Wild camomile is treated with this herbicide in the rosette stage at a rate of 1.5 kg (0.6 kg a.i.) per hectare.

Owing to the high herbicidal activity of the amine salt, the rate of use of the liquid when working with it may be reduced in aerial spraying to 25 litres, and in ground spraying to 150-300 litre/ha. The amine salt of 2,4-D has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 1150-1200 mg/kg, and for mice is 920-980 mg/kg).

Esters of 2,4-D

These herbicides are marketed in the form of emulsifiable concentrates which when mixed with water form quite stable emulsions. Droplets of the herbicide getting onto plants are firmly retained on them, penetrate into plants through their cuticles and stomas in the form of vapours, and have a stronger effect on them than salts of 2,4-D. Hence, the rate of use of 2,4-D esters is one-half to two-fifths of that of the amine salt of 2,4-D.

Esters of 2,4-D are widely used for killing dicotyledonous weeds on fields of cereal crops, corn, perennial cereal grasses, on hay fields and pastures for eradicating harmful, poisonous, and shrub vegetation, and on fallow fields for killing vegetating weeds.

On cereal crops (wheat, rye, barley, oats, millet, rice), 2,4-D esters are applied by spraying in the tillering stage, on corn in the stage of 3-5 leaves, on perennial cereal grasses also by spraying: on timothy in the stage of 2-3 leaves—the beginning of the stem extension stage, and on tall ryegrass, smooth brome grass, English blue-grass, and orchard grass in the tillering stage. Hay fields and pastures are sprayed with the herbicides in the spring and summer. On gramineous grasses, hay fields, and pastures, spraying with 2,4-D esters must be discontinued 45 days before hay cutting or before grazing cattle. It is prohibited to treat hay fields and pastures closer than 200 m to water basins.

The industry produces the following esters of 2,4-D.

The **butyl ester of 2,4-D** in the form of a 72% technical product intended for aerial applications; in the form of a 32% and 43% (butapon) emulsifiable concentrates and a 10% granulated formulation, which is recommended for treating winter wheat to kill scentless mayweeds in a mixture with ammonium nitrate and is applied at a rate of 10-12 kg (1-1.4 kg a.i.) per hectare.

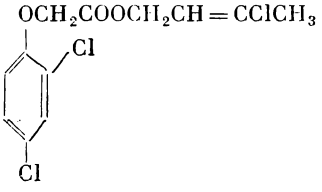
Table 25. Application of 2,4-D Esters

Crop, land	Rate of use, kg/ha								Harvest time, days
	butyl ester				low-volatile esters (C_7-C_9), 52% (technical)	octyl ester, 42% (e.c.)	chloro-crotyl ester, 44% (crotilin)	all esters, kg a.i./ha	
	72% technical	32% (e.c.)	43% (butapon)	10% (granulated)					
Wheat, rye, barley, oats	0.4-0.7	1-1.6	0.7-1.2	—	0.6-1	0.7-1.2	0.7-1.1	0.3-0.5	—
Millet	0.4-0.55	1-1.3	0.7-1	—	0.6-0.8	0.7-1	0.7-0.9	0.3-0.4	—
Sorghum	0.4-0.55	1-1.3	0.7-1	—	0.6-0.8	0.7-1	0.7-0.9	0.3-0-4	—
Rice	0.7-0.8	1.6-1.9	1.2-1.4	—	1-1.2	1.2-1.4	1.1-1.35	0.5-0.6	—
Corn	0.4-0.7	1.0-1.6	0.7-1.2	—	0.6-1	0.7-1.2	0.7-1.1	0.3-0.5	—
Timothy	0.4-0.8	1.0-1.9	0.7-1.4	—	0.6-1.2	0.7-1.4	0.7-1.35	0.3-0.6	45
Tall ryegrass, English bluegrass	0.4-0.8	1-1.9	0.7-1.4	—	0.6-1.2	0.7-1.4	0.7-1.35	0.3-0.6	45
Orchard grass	0.3-0.4	0.6-1.6	0.5-0.7	—	0.4-0.6	0.5-0.7	0.45-0.7	0.2-0.3	45
Smooth brome grass, smooth foxtail	0.3-0.7	0.6-1.6	0.5-1.2	—	0.4-1	0.5-1.2	0.45-1.1	0.2-0.5	45
Hay fields in spring	1.4	3.1	2.3	—	2	2.4	2.25	1	45
Ditto in summer	2.8	6.2	4.6	—	4	4.8	4.5	2	45
Fields to be used next year for spring crops	2.8-4.2	6.2-9.3	4.6-7	—	4-6	4.8-7.2	4.5-7	2-3	—
Fallow land	2.2	5	3.7	—	3	3.8	3.6	1.6	—
Fields with harmful and poisonous (grass, shrubs, trees) vegetation	—	7.8-18.8	6-14	—	5-11.5	6-14.3	5.7-13.6	2.5-6	45
Winter wheat	—	—	—	10-12	—	—	—	1-2	—

The **octyl ester of 2,4-D** in the form of a 42% emulsifiable concentrate.

Low-volatile esters of 2,4-D (C_7-C_9) in the form of a 52% emulsifiable concentrate.

Crotilin. The active ingredient is the γ-chlorocrotyl ester of 2,4-D:



Crotilin is marketed as a 44% emulsifiable concentrate. In comparison with the butyl ester, the low-volatile esters can be used with great success in arid regions and are a better killer of perennial offset weeds.

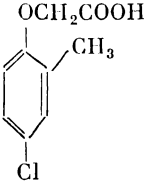
The esters of 2,4-D have a moderate and low toxicity to humans and warm-blooded animals (LD_{50} for rats in 490-1500 mg/kg).

The rates of use of 2,4-D esters on various crops and lands are given in Table 25.

The rate of use of the liquid in ground spraying is 150-300 litre/ha, and in aerial spraying 25-50 litre/ha.

MCPA (Metaxon, Agroxone, Dikotex, 2M-4Kh)

The active ingredient is 4-chloro-2-methylphenoxyacetic acid:



In the pure form, it is a white crystalline solid melting at 118-119 °C, poorly soluble in water (825 mg/litre at room temperature), and well soluble in alcohol, ether, benzene, and other organic solvents. Its sodium and potassium salts and esters with polyatomic alcohols are used as a herbicide. The formulations have a stable and pungent odour of chlorocresols.

It is marketed in the form of a wettable powder containing 80% of the sodium salt of MCPA, and in the form of an aqueous solution containing 40% of the sodium and potassium salts of MCPA.

MCPA is close to 2,4-D in its herbicidal properties and nature of action on plants, but differs in a greater selectivity and is less toxic to some cultivated plants. It is used in the same way as 2,4-D on

cereal crops, corn, on perennial grasses, and on pastures. Flax fields are treated with MCPA in the "fir-tree" stage at a height of the plants of 5-15 cm. The rate of use of the liquid in surface spraying is 300-400 litres, and in aerial spraying is 200 litre/ha.

The rates of use of MCPA formulations for various crops are given in Table 26.

Table 26. Application of MCPA

Crop, land	Rate of use, kg/ha			Conditions of use	Harvest time, days
	80% salt	40% aqueous solution	active ingredient		
Oil flax, fibre flax	0.9-1.9	1.8-4	0.7-1.5	Spraying in "fir-tree" stage at height of plants of 5-15 cm	—
Wheat, rye, barley, oats	1.3-2	2.5-4	1-1.6	Spraying in tillering stage	—
Millet	1.3-1.5	2.5-3	1-1.2	Ditto	—
Sorghum	1.3-1.5	2.6-3	1-1.2	Spraying in stage of 3-5 leaves	—
Rice	1.3-2	2.6-4	1-1.5	Spraying in stage of complete tillering	—
Timothy, smooth brome grass, meadow foxtail	1-2	2-4	0.8-1.6	Spraying in year of planting beginning from 1-2 true leaves up to stem extension stage	45
Tall ryegrass, English bluegrass	2-2.5	4.0-5	1.6-2	Ditto	45
Red clover under cover of barley	0.9-1.3	1.8-2.5	0.7-1	Spraying of clover in stage of 1-2 leaves, barley in tillering stage where allowed	45
Red clover in year of planting	0.9-1.3	1.8-2.5	0.7-1	Spraying after appearance of ternate leaf	45
Hay fields and pastures	1.3-3.5	2.5-7.5	1-2.8	Grazing of cattle not earlier than 40 days after treatment	
Potatoes (pilot application)	0.8-1.5	1.6-3	0.65-1.2	Spraying of weeds before emergence of crop	

In its toxicity for humans and warm-blooded animals, MCPA is close to 2,4-D.

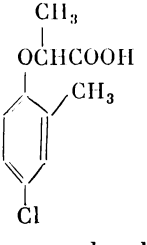
The action of herbicides that are derivatives of 2,4-D and MCPA manifests itself better on plants that are in optimal conditions of development when intensive metabolism occurs and the products of photosynthesis flow from the leaves into the stems and roots. The decisive factor intensifying or weakening the activity of regulating herbicides is the temperature. At 4-5 °C, the derivatives of 2,4-D do not virtually affect plants because the physiological processes in them are very slow, while at 10-15 °C they are attenuated. The greatest effect is achieved at 18-30 °C. In dry weather, when the flow of the assimilators from the leaves is retarded, the herbicides migrate poorly along plants, and their toxic action on weeds is weak.

3. Phenoxypropionic and Phenoxy-γ-Butyric Acid Derivatives

Phenoxypropionic acid derivatives are used to kill weeds resistant to 2,4-D and MCPA on cereal crop fields, and phenoxybutyric acid derivatives, to kill weeds on bean crop fields and on cereal crop fields with undersowing of leguminous grasses.

Mecoprop (MCPP, CMPP, Iso-Cornox)

The active ingredient is 2-(4-chloro-2-methylphenoxy) propionic acid:



Chemically pure mecoprop forms colourless odourless crystals melting at 94-95 °C (the technical product has the odour of chlorocresol), its solubility in water at 20 °C is 620 mg/litre. Its salts have a better solubility in water—the relevant figures are 250 g/litre for the sodium salt, 320 for the ammonium salt, 520 for the diethylamine salt, and 480 g/litre for the potassium salt.

Mecoprop is more persistent in the soil in comparison with 2,4-D, especially at low temperatures, therefore residues of the herbicide may be found in the soil after autumn treatments.

It is marketed in the form of a 50% aqueous solution of the amine salt with a content of 500 g of 2-(4-chloro-2-methylphenoxy) propionic acid per litre.

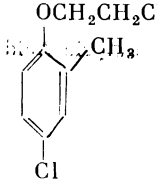
It is similar to 2,4-D and MCPA in its action on plants, but kills cleavers and common chickweed, and has a strong effect on dock, scentless mayweed, fumitory, and stinging nettle.

Mecoprop is recommended for treating cereal crops in the tillering stage at a rate of 4-6 kg (2-3 kg a.i.) per hectare. It is employed for preparing combined herbicides.

Mecoprop is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 930 mg/kg).

MCPB (2M-4KhM, Tropotox)

The active ingredient is 4-(4-chloro-2-methylphenoxy) butyric acid:



Pure MCPB is a colourless crystalline solid melting at 100 °C. It dissolves sparsely in water (44 mg/litre at room temperature) and well in organic solvents—15% in ethanol, and over 20% in acetone. The alkali metal salts of MCPB dissolve well in water.

It is marketed in the form of an aqueous solution of the sodium salt containing 80% of the active ingredient. It kills weeds sensitive to MCPA except for wild radish and white mustard. It acts weakly on cleavers, scentless mayweed, dandelion, and groundsel.

It is recommended for controlling weeds on plantings of peas, cereals with undersowing of clover and sainfoin, and also on plantings of clover and sainfoin. Peas are sprayed in the stage of three leaves at a rate of 2.5-3.8 kg of the formulation (2-3 kg a.i.) per hectare. Cereals with undersowing of clover or sainfoin are sprayed in the tillering stage at the same rate; red and white clover are treated in the year of sowing after the appearance of a ternate leaf, sainfoin—in the year of planting in the stage of 1-4 leaves; the rate of use is 2.5-3.8 kg of the formulation (2-3 kg a.i.) per hectare.

The rate of use of the liquid in spraying field crops is 200-400 litre/ha.

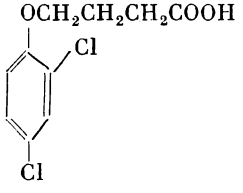
Chlorophenoxybutyric acids are by themselves physiologically inactive, but in the tissues of some plants containing enzymes of β-oxidation these acids transform into physiologically active derivatives of phenoxyacetic acid. For example, 4-(4-chloro-2-methylphenoxy) butyric acid transforms into MCPA. Many weeds contain enzymes of β-oxidation and are therefore sensitive to MCPA, whereas such cultivated plants as cereals, clover, alfalfa, and peas contain

no enzymes of β-oxidation and are therefore resistant to herbicides of this group.

MCPB is moderately toxic to humans and warm-blooded animals [LD_{50} for rats is 600 mg/kg (relative to the acid), and for mice is 700 mg/kg].

2,4-DB (Butoxon)

The active ingredient is 4-(2,4-dichlorophenoxy)butyric acid:



Pure 2,4-DB is a white crystalline solid melting at 117-119 °C. It is poorly soluble in water (46 mg/litre at 25 °C) and well soluble in organic solvents such as acetone, ethanol, and diethyl ether. In the environment, 2,4-DB decomposes into 2,4-D and 2,4-dichlorophenol. Residues in the form of 2,4-D may persist in the soil up to four months.

It is formulated as an 80% wettable powder. It is close in its herbicidal properties to MCPB. In many weeds under the action of β-oxidation, it transforms into 2,4-D.

It is recommended for spraying cereal crops: wheat, barley, and oats with the underplanting of alfalfa in the tillering stage of the cereals and after the appearance of the first ternate leaf in the alfalfa at a rate of 1.9-3.8 kg of the formulation (1.5-3 a.i.) per hectare. On solid alfalfa fields after the appearance of the first ternate leaf, the rate of use is 1.9-3.8 kg (1.5-3 kg a.i.) per hectare; on solid white clover fields, also upon the appearance of the first ternate leaf, the rate is 2.5-5 kg (2-4 kg a.i.) per hectare. The rate of application of the liquid is 200-400 litre/ha. 2,4-DB is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 700 mg/kg).

8.5.4. Carbamic and Thiocarbamic Acid Derivatives

This class of compounds includes herbicides, insecticides, and nematicides. After the synthesis in 1945 of isopropyl-N-phenylcarbamate, tests and the widespread introduction of carbamates and thiocarbamates as herbicides were begun. Their great favour is due to properties of carbamates such as their decomposition in plants and the soil, the absence of residual action, and their low toxicity to humans and warm-blooded animals.

The parent of the grouping in a carbamate molecule is carbamic acid (NH_2COOH), which is similar to amino acids, with the general formula $RCHNH_2COOH$. This provided the grounds for the assumption that carbamates can participate in the most important chemical processes of vegetating cells, i.e. play the role of antimetabolites.

It was later established that carbamates do indeed combine with amino acids, with glucose, forming glucosides, and with other compounds.

Herbicides of carbamic and thiocarbamic acids penetrate into plants through their roots, except for barban and phenmedipham, reach the vessels of the xylem and with the transpiration stream move into the vegetative and generative organs of plants. In resistant plants, they are inactivated quite rapidly, but in sensitive ones this occurs at a much slower rate. Under the action of carbamates, in young plants an intensive green colour of the leaves first appears, and then changes in the form of the generative organs and inhibition of the growth of the plants. In studying how carbamates (chlorpropham) affect the meristemic organs, it was revealed that their action is similar to that of colchicine, therefore carbamates were related to mitotic poisons. The action of carbamates disrupts the process of cell division and increases the number of chromosomes and polyploids.

It has been presumed that the reactivity of carbamate molecules in plants is due to the presence in them of the group $\diagdown$N—H, and also $\diagdown$C=O. Consequently, these molecules are capable of forming hydrogen bonds with both electropositive and electronegative components of vegetative proteins.

Subsequent research showed that carbamates inhibit photosynthesis, the fixation of CO_2 by plants, and also inhibit the process of phosphorylation. The disruption of oxidizing phosphorylation leads to diminishing of the amount of ATP and ADP in the vegetative tissues, to upsetting of the energy balance, and to disrupting of the basic metabolic reactions.

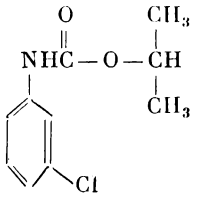
Under the influence of carbamates, the formation of RNA is disarranged and, consequently, the synthesis and metabolism of proteins are upset too.

Herbicides of this class decompose quite rapidly in the soil under the action of microbiological processes and photochemical factors. This property of carbamates provides the possibility of avoiding remote consequences when they are applied.

The data accumulated to date witness that carbamic acid esters are a relatively safe class of pesticides; they rapidly metabolize and are excreted from the organisms of mammals (N. Melnikov et al, 1977).

Chlorpropham (Chloro-IPC, Chlor-IFC)

The active ingredient is isopropyl-N-3-chlorophenylcarbamate:



It is white virtually odourless crystalline solid melting at 41.4 °C. It dissolves poorly in water (89 mg/litre at 25 °C) and well in many organic solvents. It is marketed in the form of a dark brown liquid emulsifiable concentrate containing 40% of the active ingredient and 30% of OP-7. It forms stable emulsions with water.

It decomposes in the soil during 0.6-1.2 months.

Weeds and cultivated plants have a different sensitivity to chlorpropham. Monocotyledonous gramineous plants are more sensitive to it than dicotyledonous broad-leaf weeds. Chlorpropham is a good herbicide against annual gramineous weeds such as finger grass, wild oats, bristle grass (foxtail), and barnyard grass. In plantings of carrots, this herbicide can be used to kill common chickweed. Cultivated cereals such as wheat, rye, oats, barley, and corn are sensitive to chlorpropham; among the dicotyledonous cultivated plants, flax, buckwheat, poppies, watermelons, cucumbers, pepper, tobacco, and tomatoes are sensitive to it, therefore chlorpropham must never be used on this crops. Beans, vetch, alfalfa, castor-bean plants, mustard, marrow squashes, and pumpkins are less sensitive; cotton, sunflower, potatoes, cabbage, carrots, beets, and turnips are resistant to it.

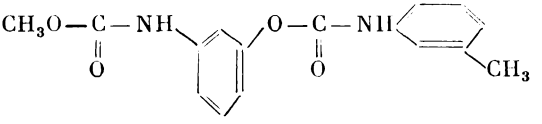
It is recommended to use chlorpropham on onion plantations by spraying the soil before the emergence of the crop at a rate of 9-15 kg of the formulation (3.6-6 kg a.i.) per hectare, and on chicory plantations at a rate of 12-16 kg (4.8-6.4 kg a.i.) per hectare. Fields of red clover are to be sprayed after the appearance of the first ternate leaf at a rate of 23-32 kg (9.2-12.8 kg a.i.) per hectare.

Chlorpropham has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 1500-3000 mg/kg).

The tolerance level of chlorpropham in carrots is 0.05 mg/kg.

Phenmedipham (Betanal)

The active ingredient is 3-methoxycarbonylaminophenyl *m*-tolylcarbamate:



The chemically pure substance forms colourless crystals melting at 143-144 °C sparsely soluble in water (3 mg/litre at room temperature) and much better in organic solvents (up to 200 g/litre).

Phenmedipham is marketed in the form of a 15.9% emulsifiable concentrate. It is a selective systemic herbicide. It is used for spraying table, fodder, and sugar beets.

Phenmedipham is not effective when incorporated into the soil. Dicotyledonous weeds are sensitive to it from the emergence stage to the formation of four true leaves, and gramineous weeds—in the stage of appearance of the first leaf.

At low temperatures and in dry weather, the action of phenmedipham on plants deteriorates; if it rains before six hours have elapsed after treatment, the effectiveness of phenmedipham also diminishes.

In hot sunny weather, spraying must be performed only in the evening. Beets coated with dew and wetted by rain must never be sprayed.

Ailing and weak plantings of beets may not be sprayed with phenmedipham.

Before treating beets with phenmedipham, the sprayers must be especially thoroughly cleaned of remnants of other herbicides (2,4-D, triazines, etc.) and washed with a 10% soda solution.

Phenmedipham kills many weeds such as shepard's purse, fat hen, common hempnettle, wild radish, charlock, and common spurrey.

Seedlings may be sprayed when two true leaves form on the beet plants. The rate of use is 6-8 kg of the formulation (1-1.35 kg a.i.) per hectare.

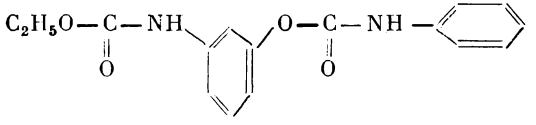
Good results in killing beet weeds are obtained by the combined use of preplanting herbicides (pyrazon, EPTC, cycloate, pebulate, etc.) and postemergent spraying with phenmedipham.

Phenmedipham is also used for spraying chicory plantations (over seedlings of the crop in the stage of 2-3 leaves) at a rate of 6.3 kg (1 kg a.i.) per hectare.

Phenmedipham decomposes in the soil during 5-6 months, and on its surface in 3-4 months. It has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 500-8000 mg/kg).

Desmedipham ***(Betanal AM, Betanex)***

The active ingredient is 3-ethoxycarbonylaminophenyl-N-phenylcarbamate:



It is a colourless crystalline solid melting at 120 °C, virtually insoluble in water (7 mg/litre at room temperature), and soluble in organic solvents.

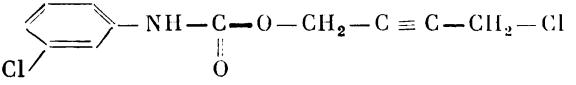
It is marketed in the form of a 16.5% emulsifiable concentrate.

Desmedipham is recommended for spraying sugar, table, and fodder beets in the stage of 1-2 pairs of true leaves at a rate of 4.8-6 kg of the formulation (0.8-1 kg a.i.) per hectare.

Desmedipham has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is over 10 000 mg/kg).

Barban (Carbyne, Chlorinat, Neoban)

The active ingredient is 4-chlorobut-2-ynyl-N-3-chlorophenylcarbamate:



In the pure form, it is a white crystalline solid melting at 75-76 °C, poorly soluble in water (11 mg/litre at 25 °C) and well in organic solvents. It is marketed in the form of a 12% emulsifiable concentrate of a dark amber colour. In addition to an emulsifier, the solution contains an anticorrosive substance. Barban is a highly selective herbicide and is employed for controlling wild oats on spring wheat and barley fields. The crops are sprayed with barban during the period from the beginning of the appearance of the second to the beginning of the appearance of the third leaf in the wild oats.

The rate of use is 3.3-5 kg of the formulation (0.4-0.6 kg a.i.) per hectare; the rate of use of the liquid is 200-400 litre/ha for ground and 50-100 litre/ha for aerial spraying.

Barban acts slowly. It suppresses the growth of wild oats and causes them to perish. The best results are obtained on more fertile and well moistened soils on which wild oats develop better and are more sensitive to barban. Investigation of the action of barban on etiolated shoots of wild oats showed that barban disrupts oxidizing phosphorylation. This leads to diminishing of the content of ADP and ATP in the vegetative tissues.

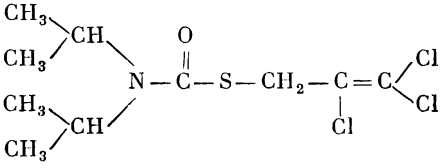
A decrease in the presence of macroergic compounds lowers the energy potential and inhibits a number of vitally important processes of metabolism.

In addition, barban disrupts the synthesis of nucleic acids and protein; inhibition of the oxidizing and photosynthesizing phosphorylation leads to the perishing of sensitive plants.

Barban is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 600-1000 mg/kg). Upon contact, it may cause irritation of the skin and mucous membranes of the eyes.

Tri-Allate (Triallate, Far-Go, Avadex BW)

The active ingredient is S-(2,3,3-trichloroallyl)di-isopropylthiocarbamate:



In the pure form, it is a liquid boiling at 165 °C, sparsely soluble in water (4 mg/litre at 25 °C) and satisfactorily in most organic solvents.

Tri-allate is marketed in the form of 10% granules and a 40% emulsifiable concentrate. It is a highly selective herbicide controlling wild oats and to a smaller extent foxtail. It does not kill other gramineous weeds.

The main way of applying tri-allate is preplanting spraying with an emulsion. Tri-allate is a volatile formulation, consequently to improve its action on weeds and reduce the losses of the herbicide due to evaporation, the soil must be well cultivated and levelled out, while after spraying the herbicide must be thoroughly incorporated to a depth of 3-6 cm.

Spring wheat, barley, flax, beets, peas, and sunflower are resistant to tri-allate. It is most effective to apply tri-allate for killing wild oats on spring wheat and barley fields.

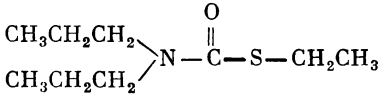
Granulated tri-allate is incorporated into the soil before planting spring wheat or barley at a rate of 10-25 kg of the formulation (1-2.5 kg a.i.) per hectare. When spraying soil before planting or before the emergence of wheat or barley, the rate of use of the herbicide is 2-4 kg (0.8-1.6 kg a.i.) per hectare.

The herbicide is applied at a rate of 2.5 kg (1 kg a.i.) per hectare for preplanting or preemergence spraying of flax to control hardy ryegrass.

Tri-allate has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 1300 mg/kg). It may cause irritation of the mucous membranes.

EPTC (Eptam)

The active ingredient is S-ethyl diprophylthiocarbamate:



In the pure form, it is a clear liquid with an aromatic odour boiling at 127 °C, sparsely soluble in water (365 mg/litre at 20 °C) and well soluble in organic solvents.

EPTC is marketed in the form of a 75% emulsifiable concentrate.

It enters plants via their roots and is recommended as a preplanting herbicide for treating soybeans, lupine, beans, and sugar beets.

EPTC kills many annual and biennial weeds, both mono- and dicotyledonous; it acts weakly on perennial weeds.

EPTC is volatile and evaporates especially rapidly from moist soil together with the moisture, therefore immediately after spraying it must be thoroughly incorporated into the soil to a depth of 3-7 cm.

EPTC is recommended for spraying soil before planting, when planting, or before the emergence of sugar, fodder, and table beets with incorporation into the soil. The rate of use is 2.7-8 kg of the formulation (2-6 kg a.i.) per hectare. The higher rates are applied on chernozem soils with a high humus content.

EPTC is also used in some regions of the USSR on fibre flax fields by spraying the soil prior to planting with incorporation into the soil for killing hardy ryegrass. The rate of use is 2.7 kg of the formulation (2 kg a.i.) per hectare. Good results in killing weeds on fields of red and white clover are obtained by the preplanting spraying of the soil with EPTC (with incoporation) at a rate of 2.7-6.7 kg of the formulation (2.5 kg a.i.) per hectare.

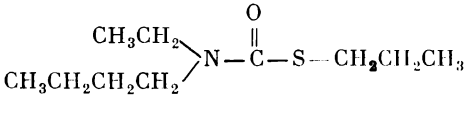
EPTC is mixed with the antidote (safener) R-25788 (N,N-diallyldichloroacetimide) to prepare eradicane, which is recommended for use on corn at a rate of up to 7 litre/ha before planting with immediate incorporation into the soil.

On sugar beet fields, the timely application of EPTC lowers the weediness of the crop when harvested by 70-80%.

EPTC has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 1630 mg/kg). The tolerance level in beets is 0.05 mg/kg.

Pebulate (Tillam)

The active ingredient is S-propyl butylethylthiocarbamate:



In the pure form, it is a clear liquid with an aromatic odour boiling at 142.5 °C (at 20 mmHg). It dissolves poorly in water (60 mg/litre at 20 °C) and well in organic solvents. It is marketed in the form of a 76.4% emulsifiable concentrate and 10% granules.

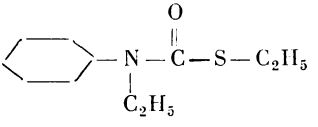
Pebulate enters plants through their roots. It is incorporated into the soil before the planting of cultivated plants with immediate covering. It kills many gramineous weeds (wild oats, bristle grass, finger grass, etc.) and annual dicotyledonous ones (fat hen, common spurrey, rough pigweed, etc.).

Pebulate is recommended for spraying with incorporation into the soil before planting, when planting, or before the emergence of sugar, fodder, and table beets at a rate of 4-6 kg of the formulation (3.1-4.6 kg a.i.) per hectare. Granulated pebulate is incorporated into the soil before planting or when planting in an amount of 30-40 kg (3-4 kg a.i.) per hectare. On hemp seed plantations, pebulate is used for spraying the soil before planting or on the third or fourth day after planting; the rate of use is 4-6 kg of the formulation (3.1-4.6 kg a.i.) per hectare, and with irrigation, 6-8 kg (4.6-6 kg a.i.) per hectare. On chernozem soils, pebulate is recommended for killing weeds on tomato plantations by incorporation into the soil before planting the seedlings at a rate of 6-8 kg (4.6-6 kg a.i.) per hectare.

Pebulate has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 1120 mg/kg). The tolerance level in vegetables, tomatoes, and sugar beets is 0.1 mg/kg.

Cycloate (Hexylthiocarbam, Ro-Neet)

The active ingredient is S-ethyl-N-cyclohexyl-N-ethyl thiocarbamate:



It is a clear liquid with an aromatic odour boiling at 145-146 °C. It dissolves poorly in water (85 mg/litre at 22 °C) and well in organic solvents such as acetone, benzene, kerosene, and methanol.

Cycloate is marketed in the form of a 72% emulsifiable concentrate. It differs from EPTC in a somewhat lower activity with respect to weeds, but in a higher selectivity with respect to sugar beets.

It is recommended for controlling weeds on plantations of sugar, fodder, and table beets by spraying the soil before planting, when planting, or before emergence with incorporation into the soil. The formulation is used at rate of 5.3-11 kg (4-8 kg a.i.) per hectare. Cycloate kills annual and biennial mono- and dicotyledonous weeds and lowers the weediness of beets when harvested by 60-70%.

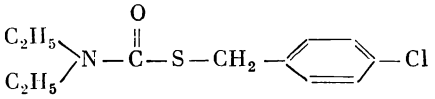
It has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 3600 mg/kg). The tolerance level in beets is 0.3 mg/kg.

Cycloate is also marketed in the form of a 70% emulsifiable concentrate (etsan), a soil herbicide killing many mono- and dicotyled-

onous annual and biennial weeds such as barnyard grass, wild oats, bristle grass, fat hen, charlock, hempnettle, and common chickweed. It is recommended for controlling weeds on plantations of sugar, table, and fodder beets by spraying the soil before planting, when planting, or before the emergence of the cultivated plants with immediate incorporation into the soil. The rate of use is 5.3-11.4 kg of the formulation (4-8 kg a.i.) per hectare. It has a low toxicity to humans and warm-blooded animals.

Thiobencarb (Benthiocarb, Bolero, Saturn)

The active ingredient is S-(4-chlorobenzyl)-N,N-diethylthiocarbamate:



It is a pale yellow liquid poorly soluble in water (about 30 mg/litre at 20 °C) and well soluble in alcohol, acetone, and xylene. It melts at 126-129 °C and solidifies at 3.3 °C.

It is marketed in the form of an emulsifiable concentrate containing 50% of the active ingredient.

Thiobencarb is characterized by its high selectivity with respect to rice and is a good herbicide for killing weeds such as barnyard grass, Japanese millet, jungle rice, green bristle grass, and annual sedges in their early stages of growth. Barnyard grass is best controlled in the stage of 1-2 leaves.

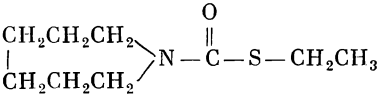
Thiobencarb penetrates into plants through their roots, but also through their leaves. It persists in the top 1-3 centimetre layer of soil and retains its activity up to 35-45 days. It is washed out from the soil in very insignificant amounts.

Thiobencarb is recommended for pilot application on rice fields by spraying the soil before planting (without incorporation), before emergence, or in the phase of 1-2 true leaves at a rate of use of 8-10 kg of the formulation (2-3 kg a.i.) per hectare.

Thiobencarb has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 1300 mg/kg).

Molinate (Ordram)

The active ingredient is S-ethyl-N,N-hexamethylenethiocarbamate:



The chemically pure product is a clear liquid with an aromatic odour boiling at 137 °C, poorly soluble in water (800 mg/litre at 21 °C) and soluble in organic solvents such as acetone, benzene, methanol, and xylene. It is stable to hydrolysis and is non-corrosive.

It is marketed in the form of a 60% emulsifiable concentrate and a 10% granulated formulation.

It enters plants through their roots, which explains why it is incorporated into the soil before planting. It kills many mono- and dicotyledonous weeds, including barnyard grass, finger grass, wild oats, fat, hen, knotweed, and dock. On fields treated with molinate, shoots of weeds appear, but they lag behind in their growth and eventually perish. Among cultivated plants, rice, wheat, barley, and sunflower are resistant to molinate.

It is recommended for killing gramineous weeds on paddy fields by preplanting spraying of the soil with incorporation by harrowing; the rate of use is 6-12 kg of the formulation (3.6-7.2 kg a.i.) per hectare.

Granulated molinate is also incorporated before planting rice in an amount of 30-60 kg of the formulation (3-6 kg a.i.) per hectare.

Tests of molinate on rice plantations in the network of toxicological laboratories of the All-Union Research Institute of Plant Protection have shown its high effectiveness. The application of molinate in doses from 6 to 9 kg/ha reduced the weediness of rice by 98-100% without lowering the thickness of stand. The yield of the rice was considerably higher than that on the control field. Granulated molinate in its action on weeds was not inferior to the emulsifiable concentrate.

Molinate is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 657 mg/kg, and for mice is 545 mg/kg); it is also moderately toxic to fish.

When incorporated into the soil in a dose of 10 kg/ha, molinate was detected in it at a depth of 30 cm and persisted for 45 days; in 15 days after treatment, it was not detected in water. When granulated molinate was applied, its content in the water of flooded rice plots was less than when the emulsifiable concentrate was used.

Molinate detracts from the organoleptic properties of water, imparting an odour of petroleum to it. The tolerance level of molinate in rice is 0.2 mg/kg.

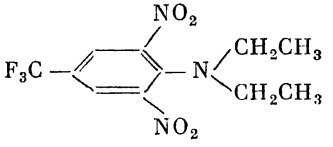
It is also recommended to use molinate on paddy fields in combination with propanil to extend the spectrum of eradicated weeds.

The maximum tolerated concentration of molinate in water is 0.025 mg/litre.

8.5.5. Aromatic Amines

Nitrofor

The active ingredient is 2,6-dinitro-N,N-diethyl-4-trifluoromethylaniline:



Pure nitrofor is a crystalline solid melting at 92-99 °C, insoluble in water, and soluble in acetone and chlorobenzene.

It is marketed in the form of a 50% wettable powder.

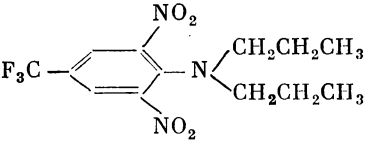
The weeds sensitive to nitrofor include barnyard grass, bristle grass, fat hen, amaranth, and common chickweed. This explains its preplanting or preemergence use being recommended with immediate incorporation into the soil to a depth of 3-5 cm.

Nitrofor has been allowed for pilot application on cabbage fields at a rate of 6-12 kg of the formulation (3-6 kg a.i.) per hectare by spraying the soil before planting the seedlings with incorporation. It is also recommended to use nitrofor on tomato plantations at a smaller rate—4-8 kg (2-4 kg a.i.) per hectare. Nitrofor is applied to fields earmarked for cotton, castor-bean plants, sunflower, and soybeans by spraying before planting, when planting, or before emergence with incorporation of the herbicide into the soil. The rates of use are the same as for cabbage plantations.

Nitrofor has a low toxicity (LD_{50} for mice is 5000, and for rats is 10 000 mg/kg).

Trifluralin (Crisalin, Treflan)

The active ingredient is 2,6-dinitro-N,N-dipropyl-4-trifluoromethylaniline:



The pure substance is an orange crystalline solid melting at 48.5-49 °C, poorly soluble in water (less than 1 mg/litre at 27 °C) and well in acetone, dichloroethane, xylene, and toluene. In a solution and in a thin layer, it decomposes under the action of sunlight with the formation of non-phytotoxic metabolites.

Trifluralin is a volatile herbicide, therefore its application must be followed by immediate incorporation into the soil. It can persist in the soil up to a year (10-15%); it decomposes more rapidly when incorporated to a small depth. In the soil, in aerobic and anaerobic conditions, it decomposes with dialkylation and the following reduction of one or both nitrogroups. It penetrates only into the roots and underground shoots of plants, but does not penetrate into the green organs, therefore its residues may be contained only in root vegetables. The mechanism of action of trifluralin is similar to that of dinitrophenols.

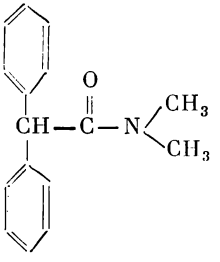
It is marketed in the form of a 25% emulsifiable concentrate. It inhibits many mono- and dicotyledonous annual and biennial weeds, but has a weak effect on perennial ones. It is recommended to use trifluralin on cotton, castor-bean plant, soybean, and sunflower fields by spraying the soil before planting, when planting, or before the emergence of the crop with the immediate incorporation into the soil, at a rate of 4-10 kg of the formulation (1-2.5 kg a.i.) per hectare; on cabbage before planting the seedlings at the same rates; on tomatoes before planting the seedlings at a rate of 4-8 kg (1-2 kg a.i.) per hectare, on coriander by spraying the soil before the emergence of the crop or together with preplanting cultivation with incorporation into the soil at a rate of 12 kg (3 kg a.i.) per hectare, on anise by preplanting or preemergence spraying at a rate of 6-8 kg (1.5-2 kg a.i.) per hectare.

Trifluralin has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 10 000 mg/kg).

8.5.6. Aromatic Carboxylic Acids and Their Derivatives

Diphenamid (Dymid)

The active ingredient is N,N-dimethyldiphenylacetamide,



In the pure form, it is a white crystalline solid melting at 134.5-135.5 °C, sparsely soluble in water (260 mg/litre at 25 °C) and better soluble in organic solvents.

It is marketed in the form of an 80% wettable powder.

Diphenamid is a soil herbicide. It penetrates into plants through their roots and persists for a long time in the soil, but its residual action does not manifest itself in the second year.

It kills many annual and biennial mono- and dicotyledonous weeds, but has a weak action on perennial ones.

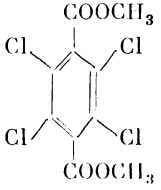
Diphenamid is recommended for pilot application to control weeds on tomato and cabbage fields by spraying the soil before sowing or before planting the seedlings. The rate of use is 5-10 kg of the formulation (4-8 kg a.i.) per hectare.

Diphenamid has a moderate and low toxicity to humans and warm-blooded animals (LD_{50} is 700-2500 mg/kg).

1. Derivatives of Dibasic Acids

Chlorthal-Dimethyl (DCPA, Dacthal)

The active ingredient is the dimethyl ester of 2,3,5,6-tetrachloroterephthalic acid:



The pure substance is a white crystalline substance melting at 156 °C, poorly soluble in water (<5 mg/litre at 25 °C), and soluble in acetone, benzene, dioxan, toluene, and xylene.

It is marketed in the form of a 50% and 75% wettable powder. It kills many annual gramineous (bristle grass, finger grass, etc.)

Table 27. Application of Chlorthal-Dimethyl

Crop	Rate of use				Method of application
	unit	active ingredient	wettable powder 50%	wettable powder 75%	
Onions, garlic, soybeans	kg/ha	8-12	16-24	10.7-16	Spraying of soil before emergence of crop
Cabbage	kg/ha	8-12	16-24	10.7-16	Spraying of soil before emergence of crop or before planting of seedlings
Fibre flax	kg/tonne	15	30	20	Dusting of seeds against hardy rye-grass in Byelorussian SSR

and dicotyledonous (fat hen, common chickweed, etc.) weeds. It does not act on common ragweed, knotweed, and perennial weeds.

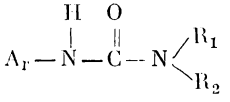
It is recommended for killing weeds on plantations of onions, garlic, soybeans, and cabbage, and in the Byelorussian SSR for dusting flax seeds against hardy ryegrass (Table 27).

Chlorthal-dimethyl has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is over 3000 mg/kg).

8.5.7. Urea Derivatives

Among urea derivatives, the most active herbicides are N-aryl-N′, N′-dialkyl ureas containing as the aromatic radical phenyl in which not over two hydrogen atoms are substituted by functional groups, and the total number of carbon atoms in the N-alkyl groups is not over five, because otherwise the activity of the compounds diminishes.

The general structure of aryl-dialkyl urea can be shown by the formula



Here A_r is phenyl, chlorophenyl, or bromophenyl, R_1 is CH_3 or OCH_3, and R_2 is CH_3, OCH_3, or H.

Herbicides such as fenuron, diuron, and monuron are distinguished by their high persistence in the conditions of the environment, a prolonged residual action in the soil, and for this reason are used most frequently as non-selective herbicides, and only in small doses as selective herbicides on certain crops.

For example, in moist clay soil in conditions of a moderately warm climate, monuron and diuron incorporated at rates of 1-3 kg/ha decompose during 3-6 months. When the dose of monuron is increased to 22-55 kg/ha, the process of its inactivation continues up to 20 months, and when diuron is incorporated at rates of 10-40 kg/ha, the process of its inactivation continues up to 6-24 months.

At present herbicides of this group such as monolinuron, linuron, and fluometuron are being synthesized that are less persistent and have a broader selectivity with respect to cultivated plants.

Most urea derivative herbicides enter plants via their roots and, moving along the xylem vessels, penetrate with the transpiration stream into the leaves, young shoots, and generative organs. The rate of their translocation depends on the rate of the ascending stream in plants. Some herbicides of this group also penetrate into the leaves when vegetating plants are sprayed.

In sensitive plants, the action of these herbicides causes weakening of the turgor, chlorosis of the leaves and their gradual dying off,

and deformation of the stems. In gramineous plants, the stems curl, and no panicles form. In all plants, the supply of water is disrupted, and the plants dry, as it were, on their roots.

Investigations have shown that in plants treated with urea derivatives, photosynthesis is inhibited; the opinion was advanced that what occurs here is suppression of the synthesis of chlorophyll, inactivation of the chlorophyl-protein complex, disruption of the system of photochemical reactions associated either with the fixation of carbon dioxide and its reduction, or with the synthesis of carbohydrates.

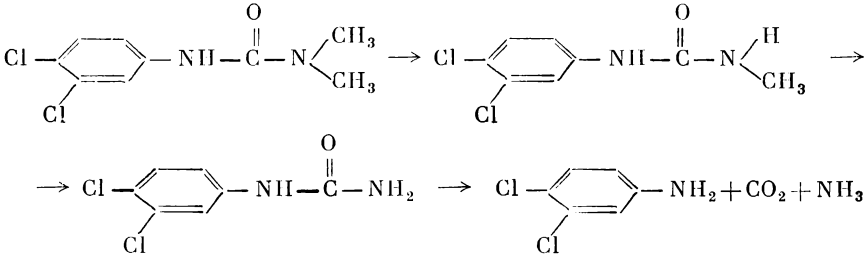
Investigations have shown that urea derivatives, like carbamates and triazines, inhibit the Hill reaction.

It has also been established that monuron inhibits cyclic phosphorylation in the presence of flavinonucleotide, the process of light absorption in photosynthesis being blocked.

According to calculations by Jagendorf, one molecule of monuron deprives at least 125 molecules of chlorophyll of their photosynthesis activity.

In plants and in the soil, urea derivative herbicides undergo involved processes leading to their decomposition and inactivation. These processes may also underlie the different resistance of plants to these herbicides. Not only the decomposition of herbicides occurs in plants, but also their combination with cell components to form complex compounds.

The process begins with dealkylation, which probably proceeds as follows:



3,4-dichloroaniline

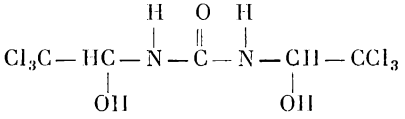
The consecutive demethylation and hydrolysis gradually lower the herbicidal activity of the formulation, which leads to its inactivation.

In soils, the process of decomposition of urea derivative herbicides occurs more rapidly in conditions of optimal moistening and at a temperature favourable for the development of microorganisms.

It has been established that the bacteria *Pseudomonas*, *Xanthomonas*, and the fungi *Penicillium*, *Aspergillus* spp. play an active role in the decomposition of these herbicides.

Dichloralurea (DCU)

The active ingredient is 1,3-bis(2,2,2-trichloro-1-hydroxyethyl)-urea:



It is a white crystalline odourless solid melting at 194 °C. It is insoluble in water, but dissolves in organic solvents. It is marketed in the form of a wettable powder containing 50% of the active ingredient, 44% of kaolin, and 6% of OP-7.

It forms a stable suspension when diluted with water. It is a preplanting herbicide killing annual gramineous weeds such as barnyard grass, green and yellow foxtail.

It is recommended for killing gramineous weeds on fields of sugar, table, and fodder beets by spraying the soil before planting, when planting, or before emergence at a rate of 8-24 kg of the formulation (4-12 kg a.i.) per hectare. It is used on tobacco plantations at the same rate by spraying the soil before planting the seedlings.

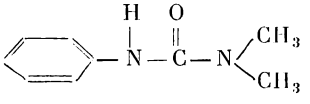
It is used on plantations of drug plants (Caucasian yam of the first, second, and third years of vegetation, and peppermint of the first and second years) by treating the soil before emergence or before growth of the crop at a rate of 30 kg of the formulation (15 kg a.i.) per hectare. On common valerian of the second year of vegetation it is applied by spraying the vegetating crop before the emergence of the gramineous weeds at a rate of 15-20 kg (7.5-10 kg a.i.) per hectare.

Dichloralurea acts on germinating weeds. Its activity lowers in dry weather. The toxicity of the herbicide persists in the soil up to 4-8 weeks, depending on the properties of the soil and the weather.

The formulation has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 6800 mg/kg). Its dust may irritate the mucous membranes of the nasopharynx. No residues of dichloralurea are tolerated in any food products.

Fenuron (Fenidim)

The active ingredient is 3-phenyl-1,1-dimethylurea:



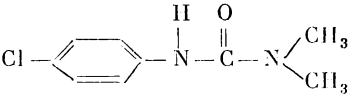
In the pure form, it is a white crystalline odourless solid melting at 133-134 °C. It dissolves poorly in water (3.85 g/litre at 25 °C) and well in alcohols, ketones, and halogen derivatives of hydrocarbons.

It is marketed in the form of an 80% wettable powder and a 25% granulated formulation. It is recommended for eradicating trees and shrubs by incorporation into the soil at a rate of 50-75 kg of the formulation (40-60 kg a.i.) per hectare in the form of an aqueous suspension. The granulated formulation is incorporated into the soil at a rate of 200-280 kg (50-70 kg a.i.) per hectare. It persists in forest soil up to five months. The use of fenuron as an arboricide is associated with its solubility in water and its penetration as a result into the zone of the root system of trees and shrubs.

Fenuron has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 7500 mg/kg).

Monuron (Chlorfenidim, Monurex)

The active ingredient is 3-(4-chlorophenyl)-1,1-dimethylurea:



It is a white crystalline substance melting at 174-175 °C. It dissolves very sparsely in water (230 mg/litre at 25 °C) and well in halogen derivatives of hydrocarbons (dichloroethane, etc.).

Technical monuron is formulated as a light gray wettable powder containing 80% of the active ingredient, 13% of kaolin, and 7% of surfactants. It is a non-selective herbicide, but in small doses is used as a selective herbicide for killing mono- and dicotyledonous annual and biennial weeds on cotton fields, grapevines, tea plantations and citrus orchards.

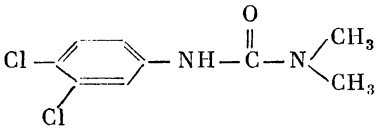
Monuron dissolves poorly in water, therefore it remains in the top layer of the soil and does not harm trees and shrubs with a deep root system. Monuron is used for the preemergent spraying of cotton at a rate of 0.9-1.8 kg of the formulation (0.7-1.4 kg a.i.) per hectare.

In pip fruit orchards and on grapevines (above three years old), monuron is applied by spraying the soil in the early spring, before emergence of the weeds, at a rate of 3-4 kg (2.4-3.2 kg a.i.) per hectare. In autumn spraying on grapevines (above three years old), the dose is 1.3-6 kg (1-4.8 kg a.i.) per hectare. The same dose (1-4.8 kg a.i./ha) is used for early spring spraying on tea plantations before the emergence of the weeds. For the complete killing of weeds, monuron is applied at a rate of 20 kg and more per hectare. In this case, its action continues at least two years.

Monuron is used to prepare various herbicide mixtures. It has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 3600 mg/kg).

Diuron (Dichlorfenidim, Karmex, Unidron)

The active ingredient is 3-(3,4-dichlorophenyl)-1,1-dimethylurea:



It is a white odourless crystalline solid melting at 158-159 °C. It dissolves poorly in water (42 mg/litre at 25 °C) and sparsely in hydrocarbons (for example, its solubility in acetone is 5.3 g/litre at 27 °C).

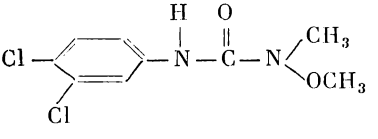
It is marketed in the form of a wettable powder containing 80% or 50% of the active ingredient. It is a good killer of many mono- and dicotyledonous weeds such as bristle grass, barnyard grass, amaranth, fat hen, and black nightshade. It is applied on cotton fields by spraying the soil when sowing or before the emergence of the crop (overall and band application). The rate of use of the 80% wettable powder is 0.5-2 kg (0.4-1.6 kg a.i.) per hectare. It is also recommended for early spring application in pip fruit orchards, on currant, gooseberry, and raspberry plantations at a rate of 3-5 kg (2.4-4 kg a.i.) per hectare, and in citrus orchards (over four years old) also by spraying the soil early in the spring before emergence of the weeds at a rate of 3-5 kg (2.4-4 kg a.i.) per hectare.

In higher doses, diuron is employed as a non-selective herbicide. In this case, it persists in the soil up to 6-24 months. Owing to its slight solubility, the herbicide remains after being sprayed in the top layer of the soil. The 50% wettable powder is used on the same crops at a rate of 0.8-8 kg/ha.

Diuron has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 3500 mg/kg). Its tolerance level in cotton-seed oil is 0.05 mg/kg.

Linuron (Afalon, Lorox)

The active ingredient is 3-(3.4-dichlorophenyl)-1-methoxy-1-methyl-urea:



It is a white odourless crystalline solid melting at 93-94 °C. It dissolves poorly in water (75 mg/litre at 25 °C) and well in organic solvents.

Table 28. Application of 50% Wettable Powder of Linuron

Crop	Rate of use, kg/ha		Way of application
	formulation	active ingredient	
Corn, soybeans	4-6	2-3	Spraying of soil before planting, when planting, or before emergence of crop
Potatoes, coriander	4-6	2-3	Spraying of soil before emergence of crop
Coriander	4-8	2-4	Spraying of crop in stage of 2-3 true leaves combined with preemergence and postemergence harrowing
Carrots	1.6-6	0.8-3	Spraying of soil before emergence or over seedlings. The carrots may be used for food or fodder only in four months after treatment
Lupine, lentils	3-4	1.5-2	Spraying of soil before planting or before emergence of crop
Peavine	3-5	1.5-2.5	Ditto
Vetch	3	1.5	Ditto
Beans	3-4	1.5-2	Spraying of soil 2-3 days before emergence of crop
Fodder beans	3-5	1.5-2.5	Spraying of soil before emergence of crop
Ornamental roses	6-8	3-4	Spraying of soil before appearance of leaves on plants with protection of the plants
Everblooming pinks	1.5-2	0.75-1	Spraying of soil before emergence of weeds with protection of the crop
Ammi visnaga	2-3	1-1.5	Spraying of crop in rosette phase
Peppermint	3-8	1.5-2	Spraying of soil before growth of seedlings of cultivated plants
Hemp (seed plantations)	8	4	Spraying of soil before planting or on the third or fourth day after planting (before emergence) for killing common ragweed

It is marketed in the form of a 50% wettable powder. Owing to its poor solubility in water, linuron accumulates in the top layer of the soil. It is good against annual gramineous and dicotyledonous weeds such as bristle foxtail grass, finger grass, barnyard grass, knotweed, ragweed, fat hen (pigweed), and rough pigweed. Depending on the properties and moisture content of the soil, linuron is inactivated in it in three or four months and does not harm the following crops in the crop rotation.

In a dose of 4-6 kg/ha with preemergent incorporation, it does not harm corn, cotton, flax, peas, beans, carrots, potatoes, soybeans,

and the crops following them in the crop rotation. It is widely used as a preplanting and preemergence herbicide on many crops including corn, potatoes, carrots, coriander, and on plantations of leguminous and drug crops by spraying the soil with a suspension of the herbicide. The rates of use and the ways of applying linuron are given in Table 28.

The pilot use of linuron is allowed on fibre flax fields for killing hardy ryegrass by preemergent spraying. The rate of use of the liquid in surface spraying is 200-400 litre/ha.

It is prohibited to use carrots from treated plots for food or fodder purposes until four months have elapsed from the time of treatment.

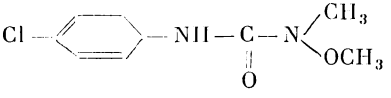
No residues of linuron are tolerated in carrots. Its tolerance level in potatoes is 0.1 mg/kg.

Linuron is also recommended for spraying the soil before growth of the crop on plantations of common valerian in the second year of vegetation at a rate of 4 kg of the formulation (2 kg a.i.) per hectare and of peppermint for spraying the soil before emergence of the crop in the first year or sprouting of the second year crop at a rate of 3-8 kg (1.5-4 kg a.i.) per hectare.

Linuron has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 1500 mg/ha).

Monolinuron (Aresin, Premalin)

The active ingredient is 3-(4-chlorophenyl)-1-methoxy-1-methylurea:



The pure substance is a white odourless crystalline solid melting at 75-78 °C and soluble in ethanol, acetone, benzene, and other organic solvents except saturated hydrocarbons.

Its solubility in water is 735 mg/litre at 25 °C.

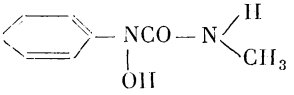
It is marketed in the form of a 50% wettable powder. When incorporated into the soil, it kills many mono- and dicotyledonous weeds, especially well during their sprouting.

It is recommended for killing weeds on potato fields by preemergent spraying of the soil at a rate of 3-6 kg of the formulation (1.5-3 kg a.i.) per hectare; on fibre flax fields for killing hardy rye-grass by preemergent spraying of the soil at a rate of 1-1.8 kg (0.5-0.9 kg a.i.) per hectare.

Monolinuron has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 2250 mg/kg). The tolerance level in potatoes is 0.1 mg/kg.

Meturin

The active ingredient is 3-phenyl-3-hydroxy-1-methylurea:



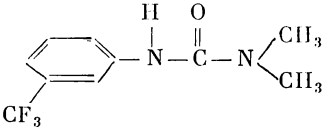
In the pure form, it is a white crystalline solid melting at 132 °C. It dissolves poorly in water, and well in organic acids.

It is marketed in the form of an 80% wettable powder. It is a selective herbicide for killing annual weeds on potato fields. It is recommended for pilot use for preemergent spraying of the soil at a rate of 4-6 kg of the formulation (3.2-4.8 kg a.i.) per hectare. Meturin persists in the soil two or three months, accumulating in the top 10-centimetre layer.

Meturin has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 5000 mg/kg). The tolerance level in potatoes is 0.1 mg/kg.

Fluometuron ***(Cotoran, Lamex)***

The active ingredient is 1,1-dimethyl-3-(3-trifluoromethylphenyl)-urea:



It is a white crystalline solid melting at 163-164 °C. It dissolves poorly in water (105 mg/litre at 20 °C), and well in organic solvents (acetone, ethanol, and 2-propanol).

It is marketed in the form of an 80% wettable powder. It is good for application against both mono- and dicotyledonous annual and biennial weeds on cotton fields. It persists in the soil from two to five months.

It is recommended for spraying the soil before planting, when planting, or before the emergence of the cotton at a rate of 1.6-3.5 kg of the formulation (1.3-2.8 kg a.i.) per hectare.

In band application, the rate of use of the herbicide is halved.

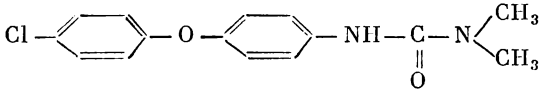
On plantations of common plantain, fluometuron is recommended for spraying the soil in 1-5 days after planting or early in the spring before sprouting of the plants begins at a rate of 1.9-2.5 kg of the formulation (1.5-2 kg a.i.) per hectare. The rate of use of the liquid is 200-400 litre/ha.

On peppermint, it is recommended to spray the soil before emergence of the crop in the first year of vegetation or before sprouting of the plants in the second year of vegetation at a rate of 6 kg (4.8 kg a.i.) per hectare; on mound lily yucca, the rate is 5-6 kg (4-4.8 kg a.i.) per hectare in the same periods.

Fluometoran has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 6000 mg/kg). The tolerance level in cottonseed oil is 0.1 mg/kg.

Chloroxuron (Chloroxifenidim, Tenoran)

The active ingredient is 3-[4-(4-chlorophenoxy)-phenyl]-1,1-dimethylurea:



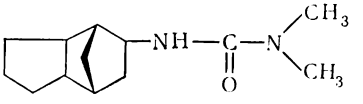
In the pure form, it is a white crystalline solid melting at 151-152 °C. It dissolves poorly in water (3.7 mg/litre at 20 °C), and well in acetone and chloroform.

It is marketed in the form of a 50% wettable powder. It kills many annual and biennial dicotyledonous weeds, acts considerably more weakly on gramineous weeds and dicotyledonous perennials. It is recommended for pilot use on carrot fields by preemergent spraying of the soil at a rate of 6-12 kg of the formulation (3-6 kg a.i.) per hectare, and also for killing weeds on plantations of everblooming pinks by spraying before emergence of the weeds with protection of the crop at a rate of 10-12 kg (5-6 kg a.i.) per hectare.

Chloroxuron has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 1000 mg/kg). The tolerance level in carrots is 0.02 mg/kg.

Norea (Noruron, Herban)

The active ingredient is 3-(hexahydro-4,7-methaneindan-5-yl)-1,1-dimethylurea:



It is a white crystalline substance melting at 168-169 °C, poorly soluble in water (150 mg/litre), and well soluble in acetone and ethanol.

It is marketed in the form of an 80% wettable powder.

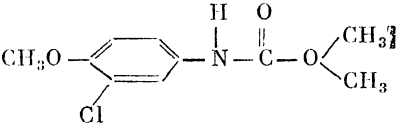
Norea is a soil herbicide penetrating into a plant through its roots, therefore its action depends substantially on the moisture content of the soil and its absorptivity.

Norea kills many dicotyledonous and annual gramineous weeds and is recommended as a preemergence herbicide on cotton fields; it is used for spraying the soil at a rate of 3-6 kg of the formulation (2.4-4.8 kg a.i.) per hectare.

Norea has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 2000 mg/kg).

Metoxuron (Deftor, Dosanex)

The active ingredient is 3-(3-chloro-4-methoxyphenyl)-1,1-dimethylthiourea:



In the pure form, it is a white odourless crystalline powder melting at 126-127 °C, poorly soluble in water (678 mg/litre at 23-24 °C) and soluble in acetone and hot ethanol. It is stable in storage, but decomposes in the soil and in plants, and this process begins with stepwise demethylation.

It is marketed in the form of an 80% wettable powder. It enters plants via their leaves and roots. The most resistant to metoxuron among cultivated plants are wheat, barley, and carrots, while rye, oats, celery, and parsley are sensitive to it.

Metoxuron kills many dicotyledonous weeds such as fat hen, shepard's purse, hempnettle, knotweed, wild radish, and field pansy, and gramineous weeds such as Japanese barnyard millet, wild oats, bristle grass, and meadow foxtail.

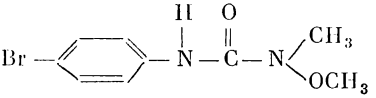
Metoxuron is allowed for pilot use on carrot fields at a rate of 3.8-7.5 kg of the formulation (3-6 kg a.i.) per hectare by spraying the soil before the emergence of the cultivated crop or in the stage of 1-2 true leaves; it is prohibited to use the carrots for food or fodder purposes until four months elapse after treatment. Metoxuron may be used on fields of spring wheat and barley by spraying in the stage of 2-3 leaves at a rate of 3.1-5.5 kg (2.5-4.4 kg a.i.) per hectare.

Metoxuron decomposes in the soil in two or three months, while its residues are detected in the carrots in very small amounts (0.03-0.15 mg/kg).

Metoxuron has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 1600-2000 mg/kg).

Metobromuron ***(Patoran)***

The active ingredient is 3-(4-bromophenyl)-1-methoxy-1-methylurea:



It is a white crystalline solid melting at 95.5-96 °C, poorly soluble in water (330 mg/litre at 20 °C), and well in acetone, ethanol, and chloroform.

It is marketed in the form of a 50% wettable powder. It penetrates into plants via their roots. Its persistence in the soil is low. It kills many dicotyledonous annual and biennial weeds, and also annual meadow grass, barnyard grass, and ryegrass.

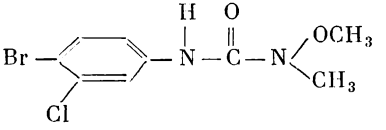
Metobromuron is recommended for killing weeds on potato fields by spraying the soil before the emergence of the crop at a rate of 4-5 of the formulation (2-2.5 kg a.i.) per hectare. The potatoes may be used not earlier than in three months after introduction of the herbicide.

Metobromuron is also used on plantations of common valerian by spraying the soil before the emergence of the crop or before the sprouting of plants in the second year of vegetation at a rate of 3-4 kg (1.5-2 kg a.i.) per hectare.

Metobromuron has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 3000 mg/ha).

Chlorbromuron ***(Maloran)***

The active ingredient is 3-(3-chloro-4-bromophenyl)-1-methoxy-1-methylurea:



Pure chlorbromuron is a colourless or yellowish odourless crystalline powder melting at 97 °C. It dissolves poorly in water (50 mg/litre) and well in acetone, dimethyl sulphoxide, and chloroform.

It is marketed in the form of a 50% wettable powder. It enters plants via their leaves and roots, therefore it is a good herbicide against sprouting weeds and their shoots. Many dicotyledonous annual and biennial weeds are sensitive to chlorbromuron including amaranth, ragweed, fat hen, shepard's purse, knotweed, wild radish, charlock, common spurrey, common chickweed, and field pennycress,

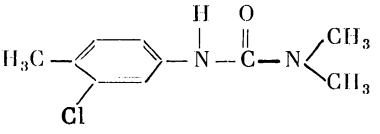
and among gramineous weeds—bristle grasses. Foxtail, wild oats, bedstraw, and field pansies are resistant to it.

Chlorbromuron is recommended for pilot use on carrot fields by spraying the seedlings in the stage of 1-3 true leaves at a rate of 3-5 kg of the formulation (1.5-2 kg a.i.) per hectare, and also on plantations of wild camomile by spraying the crop in the rosette stage at a rate of 2.5-3 kg (1.25-1.5 kg a.i.) per hectare.

Chlorbromuron has a low toxicity to warm-blooded animals (LD_{50} for rats is 4280 mg/kg).

Chlorotoluron ***(Chlortoluron, Dicuran, Tolurex)***

The active ingredient is 3-(3-chloro-4-methylphenyl)-1,1-dimethylurea, also known as 3-(3-chloro-*p*-tolyl)-1,1-dimethylurea:



It forms colourless odourless crystals melting at 147-148 °C, poorly soluble in water (70 mg/litre at 20 °C) and soluble in ethanol and acetone.

It is marketed in the form of an 80% wettable powder. It is a good killer of many di- and monocotyledonous annual and biennial weeds.

Chlorotoluron is recommended for spraying plantations of oil-bearing poppy in the stage of 4-6 leaves at a rate of 3 kg of the formulation (2.4 kg a.i.) per hectare.

Chlorotoluron has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is over 3000 mg/kg).

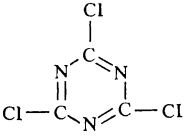
8.5.8. Derivatives of ***1,3,5-Triazines***

Triazine derivatives include herbicides having a broad spectrum of action that kill many species of weeds, and also herbicides with a narrow selectivity. Triazine derivatives are characterized by both a systemic and a contact action. The phytotoxic action of triazines in the soil continues from a few days to several years and is due to the structure and physicochemical properties of these herbicides.

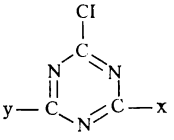
Derivatives of 1,3,5-triazines are obtained from cyanuric chloride by substitution of the chlorine atoms with various functional groups.

The structure of 1,3,5-triazine derivatives is shown below:

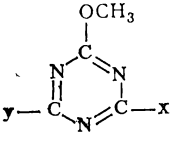
(I)-Cyanuric chloride



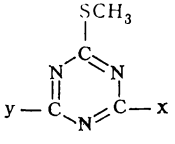
(II) Chlorotriazines



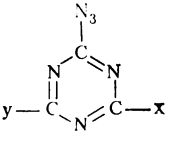
(III) Methoxytriazines



(IV) Methylthiotriazines



(V) Azidotriazines



The first group of 1,3,5-triazines includes chlorine-substituted ones (compound II), among which are simazine, atrazine, and propazine. The second group (compound III) includes methoxy-substituted triazines: simeton, atraton, prometon; this group is distinguished by its considerably higher solubility in water. The third group (compound IV) includes simetryne, desmetryne, ametryne, prometryne. The fourth group (compound V) includes aziprotryne. All tri-

Table 29. Structure and Selected Properties of Herbicides—Derivatives of 1,3,5-Triazines

Group	Substitutes in position		Formulation	Solubility in water, mg/litre	LD_{50} for rats, mg/kg
	x	*y*			
Chlorotriazines	NH—C_2H_5	NH—C_2H_5	Simazine	5	5000
	NH—C_2H_5	NH—C_3H_7 (iso)	Atrazine	33	3080
	NH—C_3H_7 (iso)	NH—C_3H_7 (iso)	Propazine	9	5000
Methoxytriazines	NH—C_2H_5	NH—C_2H_5	Simeton	3200	535
	NH—C_2H_5	NH—C_3H_7	Atraton	1800	1465-2400
	NH—C_3H_7 (iso)	NH—C_3H_7 (iso)	Prometon	750	2980
Methylthiotriazines	NH—CH_3	NH—C_3H_7 (iso)	Desmetryne	500	1390
	NH—C_2H_5	NH—C_2H_5	Simetryne	450	1830
	NH—C_2H_5	NH—C_3H_7 (iso)	Ametryne	185	1110-2250
	NH—C_3H_7 (iso)	NH—C_3H_7 (iso)	Prometryne	48	3750
Azidotriazines	S—CH_3	NH—C_3H_7 (iso)	Aziprotryne	75	5833

azine herbicides have a low toxicity to humans and warm-blooded animals (Table 29).

Triazine derivatives penetrate into plants mainly through their roots and are therefore used as soil herbicides.

Under the influence of triazine herbicides, the growth of sensitive plants stops, and their leaves become chlorotic, which points to the inhibition of photosynthesis.

It has been established experimentally that triazines destroy chloroplasts.

Many investigators have shown in recent years that triazines inhibit the photolysis of water and the Hill reaction.

Since the Hill reaction is a constituent part of non-cyclic photosynthetic phosphorylation, its inhibition makes the formation of ATP impossible in the process of phosphorylation, and the reduction of NADPH does not occur (V. Ladonin). When these substances, rich in energy, are lacking, the assimilation of carbon dioxide may discontinue. As a result of the composite action of triazines on photosynthesis, and inhibition of respiration, the energy balance of the plants deteriorates, and the reactions requiring energy in the overall process stop. In addition, under the influence of triazines, the functions of mineral nutrition and the synthesizing processes in the roots are sharply and irreversibly disrupted. Water metabolism and respiration are upset, and the enzymes are inactivated, which inevitably affects the general vital activities of the plants and leads to their perishing.

Triazine derivatives undergo metabolism in plants under the action of the enzyme systems.

It has been assumed (W. Roth) that plants have two systems inactivating triazines. The first of them, containing phenol compounds, reacts directly with the herbicide as soon as it enters the roots, causing a slight transformation of the triazine with the formation, probably, of a non-toxic complex. The second (polyphenoloxidase) system causes ring breakage and the evolution of carbon dioxide. It is exactly the differences in the activity of these systems that underlie the different ability of plants to metabolize triazines to carbon dioxide.

Triazine derivatives retain their phytocidal action in the soil for quite a long time; for example, simazine introduced into clay soil at a rate of 4 kg/ha persists up to 5-7 months, and at a rate of 10 kg/ha—up to 15 months.

The persistence in the soil of chlorotriazines—simazine, atrazine, and propazine—is longer, while methylthiotriazines decompose more rapidly. For instance, the persistence of prometryne in the soil is limited to one season, and its use is not dangerous to the following crops. Economical harm may be caused by the phytotoxicity of chlorotriazines—atrazine, simazine, and propazine.

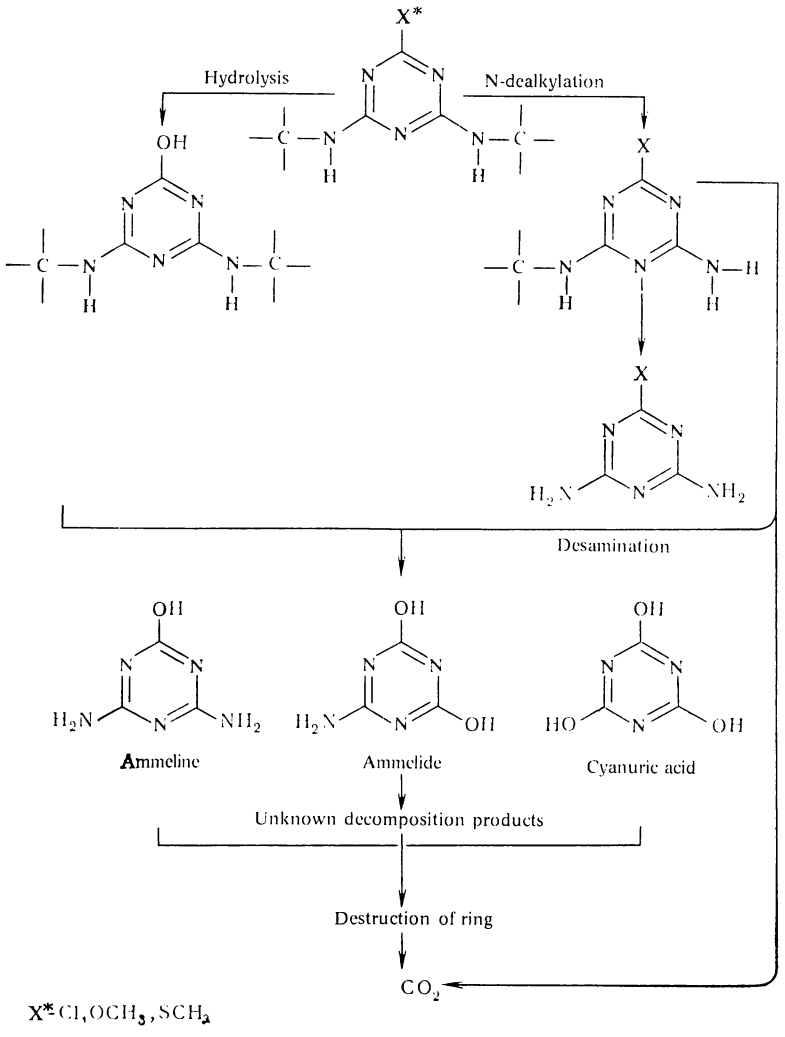


Fig. 15. Diagram showing how triazines decompose in the soil (after H. Esser): X* is Cl, OCH_3, or SCH_3

The rate of inactivation of 1,3,5-triazines in the soil depends on the genetic type of the soil. In the order of their diminishing ability to inactivate atrazine, soils can be arranged as follows: red soil, soddy-podzolic soil, soil of the subtropics, mountain meadow chernozem soil, cinnamonic calcareous soil, meadow-boggy soil, mountain-forest brown soil, and chestnut soil.

Owing to their sparse solubility in water, triazines are retained in the top layer of the soil at a depth of 0-10 cm and experience the usual processes of action: photo-decomposition, absorption by soil colloids and plants, and to a smaller extent evaporation and washing out. The soil microorganisms are the chief decomposing factor. The fungi *Aspergillus*, *Fusarium*, *Penicillium*, etc., and the bacteria *Pseudomonas sp.*, *Corynebacterium sp.*, etc. participate in this process.

The decomposition of triazines in the soil also follows the path of dealkylation and dechlorination through the formation of ammeline, ammelide, and cyanuric acid.

This process occurs more actively at a higher moisture content and low values of the pH, and also at elevated temperatures; in these conditions, the chemical hydrolysis of the triazines becomes more intense. The inactivation of triazines in the soil is also intensified under the influence of soil cultivation, irrigation, and the incorporation of organic and mineral fertilizers.

A diagram showing how triazines are decomposed in the soil is given in Fig. 15.

It is important to stress that triazines do not inhibit beneficial microflora, nitrogen-fixing and nitrifying bacteria. Consequently, they do not harm the transformation of nitrogen compounds in the soil.

The action of triazine derivatives on sensitive plants in toxic doses causes disruption of photosynthesis, decomposition of the chloroplasts, inhibition of water photolysis, diminishing of the carbohydrate content, suppression of respiration of the tissues, and a change in the activity of the enzymes leading to a predomination of hydrolytic processes over synthesizing ones.

In such plants, there is a reduction in the content of protein nitrogen and an increase in the content of non-protein forms including free ammonia nitrogen, the synthesis of DNA and RNA decreases, and organic phosphorus compounds soluble in acids and alcohols accumulate. The absorption of the main elements of nutrition is weakened and stops, the growth of the plants is retarded, the leaves lose their colour, and the plants lose their turgor, wilt, and dry up.

Simazine (Gesatop, Primatol S, Simadex)

The active ingredient is 2-chloro-4,6-di(ethylamino)-1,3,5-triazine:

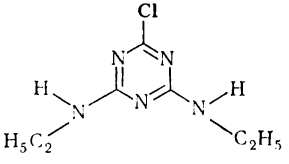


Table 30. Application of Simazine

Crop	Rate of use, kg/ha			Way of application
	formulation		active ingredient	
	50%	80%		
Corn	3-12	1.9-7.5	1.5-6	Spraying of soil before planting, when planting, or before emergence of crop
Pip, stone, and citrus fruits, currants, gooseberries, raspberries, grapevines (over 3 years old), tea plantations	4-8	2.5-5	2-4	Spraying of soil in early spring before emergence of weeds
Ditto (except tea plantations)	6-12	3.75-7.5	3-6	Spraying of soil in autumn after ploughing
Strawberries	1.6-3	1-1.85	0.8-1.5	Spraying of soil in early spring before leaves begin to grow in crop
Winter wheat, winter rye (in regions where permitted)	0.5	0.3	0.25	Preemergence spraying
Cinnamon rose (beginning from 3 years old)	8-10	5-6.25	4-5	Directed spraying before weed emergence in early spring or in late autumn after defoliation
Caucasian yam in 1st year of vegetation	6	3.75	3	Preemergence spraying of soil
Ditto, in 2nd and 3rd years	8	5	4	Spraying of soil before sprouting of crop
Volatile oil-bearing roses	6-12	3.75-7.5	3-6	Directed spraying in spring before sprouting of crop or in late autumn when applied every other year
Lavender	4-12	2.5-7.5	2-6	Ditto
Lupine	1.5	0.9	0.75	Preemergence spraying

It is a white crystalline solid melting at 225-227 °C, poorly soluble in water (5 mg/litre at 20-22 °C) and sparingly soluble in organic solvents such as chloroform, methanol, and ethyl ether.

It is marketed in the form of a white wettable powder containing 50 or 80% of the active ingredient. It is used as a selective preplanting herbicide on corn fields.

Simazine enters plants through their roots, therefore it must be incorporated into the moist layer of the soil in the zone of sprouting weeds. Simazine kills annual and biennial weeds when they

sprout and at a young age. To kill amaranth, fat hen, black bindweed, bushy knotweed, hempnettle, and green bristlegrass in the germination stage (2-3 leaves), it is sufficient to introduce 4-8 kg of simazine per hectare. The dose is increased when these weeds are greatly developed. The dose of the herbicide is also increased to kill perennial weeds such as common horsetail, Canadian thistle, field sowthistle, and couch grass.

Simazine migrates poorly in the soil and remains at a depth up to 10 cm. It decomposes slowly and has a prolonged persistence. Consequently, fields treated with simazine may not be used in the following years to grow plants sensitive to it such as oats, barley, spring and winter wheat. Millet, sorghum, peas, turnips, and potatoes are less sensitive to simazine. It is best of all to use large doses of simazine on a field with repeated planting of corn, which is resistant to this herbicide.

In corn plants, simazine is rapidly decomposed under the action of the enzyme peroxidase at a high activity of the polyphenols.

Since simazine migrates poorly in the soil, it is recommended for application in the inter-row spacings of row crops, in orchards and on grapevines. The decomposition of simazine in the soil is accelerated when it is cultivated. The doses of simazine are established depending on the mechanical composition of the soil and on the content of humus in it. When growing corn on light soddy-podzolic soils, it is sufficient to incorporate 1.5-2 kg, on heavier soils (medium and heavy loams)—2-3 kg, and on chernozems—over 3-6 kg/ha with the liquid used at a rate of at least 400-500 litre/ha.

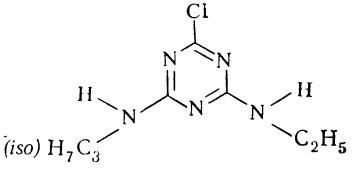
In arid regions, simazine should be applied immediately after melting of the snow, or even in the autumn.

The rates of use of simazine and the ways of applying it are given in Table 30.

Simazine has a low toxicity to humans and warm-blooded animals (see Table 29). The tolerance level in grapes is 0.05, in fruits is 0.2, and in cereals is 1 mg/kg.

Atrazine (Vectal SC)

The active ingredient is 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine:



In the pure form it is a colourless, odourless crystalline solid melting at 175 °C. It dissolves poorly in water (28 mg/litre at 20 °C) and better in ethyl ether, methanol, and chloroform.

It is marketed in the form of a white or grayish wettable powder containing 50% of the active ingredient. It is a selective herbicide and is in great favour for killing weeds on corn fields, coriander plantations, in orchards, and on grapevines.

In comparison with simazine, atrazine dissolves somewhat better in water and has a higher physiological activity. It penetrates into plants via their roots and leaves, therefore it may be applied before the emergence of weeds and to their shoots, spraying them with a suspension. Atrazine is good for controlling weeds in drier conditions than simazine. The rate of use of atrazine is 1-2 kg/ha on soddy-podzolic soils and 3-4 kg/ha on chernozems, depending on the mechanical composition of the soil. The rates of use of atrazine and the ways of applying it are given in Table 31.

Table 31. Application of Atrazine

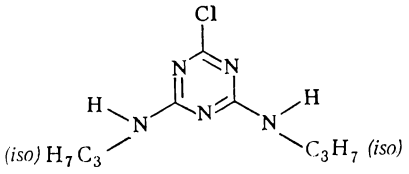
Crop	Rate of use, kg/ha		Way of application
	50% formulation	active ingredient	
Corn	3-8	1.5-4	Spraying of soil before planting (with incorporation), when planting, or before emergence of crop
Coriander	3-4	1.5-2	Preemergence spraying of soil
Fruit crops (pip), grapevines (over 3 years old), currants, gooseberries, raspberries	4-12	2-6	Spraying of soil in early spring before emergence of weeds
Ditto	12-16	6-8	Spraying of soil in autumn after harvesting
Caucasian yam	6	3	Spraying of plants of 1st, 2nd, and 3rd year of vegetation before emergence or sprouting
Fields earmarked only for corn next year	6	3	Spraying of soil in autumn after ploughing (in arid regions)

The rate of use of water for surface spraying is 400-500, and for aerial spraying is 100 litre/ha.

Atrazine has a low toxicity to humans and warm-blooded animals (see Table 29). Its tolerance level in fruits and vegetables is 0.1, in cereals is 0.25, and in meat and eggs is 0.02 mg/kg.

Propazine (Gesamil, Milogard)

The active ingredient is 2-chloro-4,6-di(isopropylamino)-1,3,5-triazine:



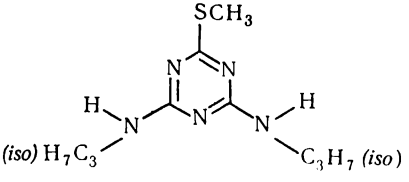
It is a white crystalline solid melting at 212-214 °C, poorly soluble in water (8.6 mg/litre at 20 °C) and sparingly in organic solvents such as acetone, dichloroethane, ethanol, and ethyl ether.

It is marketed in the form of a 50% wettable powder. It kills annual and biennial gramineous and dicotyledonous weeds. It is incorporated into the soil during germination of the seeds and at a very early age of the weeds. It is recommended for killing weeds on sorghum, millet, coriander, and carrot fields by preemergence spraying of the soil at a rate of 3-6 kg of the formulation (1.5-3 kg a.i.) per hectare, the liquid being used at rate of 400-500 litre/ha. Propazine has a low toxicity to humans and warm-blooded animals (see Table 29).

No residues of propazine in carrots are tolerated.

Prometryne (Prometryn, Gesagard, Caparol)

The active ingredient is 2,4-di(isopropylamino)-6-methylthio-1,3,5-triazine:



It is a white crystalline solid melting at 118-120 °C, poorly soluble in water (48 mg/litre at 20 °C) and moderately soluble in organic solvents.

It is marketed in the form of a 50% wettable powder. It enters plants via their leaves and roots, acts on the shoots of sensitive weeds, and kills gramineous and dicotyledonous weeds.

It persists in the soil up to three months. It is recommended for the preplanting and preemergence spraying of the soil on cotton,

coriander, sunflowers, carrots, many leguminous and drug crops, on potatoes and vegetable crops such as celery, parsley, and dill. The rates of use and ways of applying prometryne are given in Table 32.

Table 32. Application of Prometryne

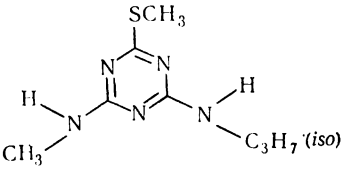
Crop	Rate of use, kg/ha		Way of application
	50% wettable powder	Active ingredient	
Cotton:			
overall application	3-5	1.5-2.5	Spraying of soil before planting, when planting, or before emergence of crop
band application	1.3-2.5	0.65-1.25	
Peas, soybeans, castor-bean plants, coriander, garlic	3-5	1.5-2.5	Preemergence spraying of soil
Sunflowers	2-6	1-3	Spraying of soil before planting, when planting, or before emergence of crop
Coriander	4-8	2-4	Spraying of crop in stage of 2-3 true leaves combined with preemergent or postemergent harrowing
Potatoes	3-5	1.5-2.5	Preemergence spraying of soil
Carrots	2-5	1-2.5	Spraying of soil before planting, before emergence, or over shoots (in stage of 1-2 true leaves)
Celery, parsley, dill	3-5	1.5-2.5	Postemergence spraying
Beans	3	1.5	Spraying of soil 2-3 days before emergence of crop
Lupine	3-5	1.5-2.5	Spraying of soil (with incorporation when cultivating) before planting or before emergence of crop (without incorporation)
Vetch	3	1.5	Ditto
Lentils	3-4	1.5-2	Ditto
Peavine	3-5	1.5-2.5	Ditto
Fodder beans	3-4	1.5-2	Preemergence spraying of soil (without incorporation)
Clary sage, peppermint, lavender	6	3	Spraying of soil in spring before plants begin to sprout with incorporation of herbicide by harrowing
Wild camomile	2.5-3	1.25-1.5	Spraying of crop in rosette stage

It is prohibited to use carrots for food or fodder until four months have elapsed after the application of prometryne, and potatoes until three months have elapsed.

Prometryne has a low toxicity to humans and warm-blooded animals (see Table 29). No residues of prometryne are tolerated in carrots. The tolerance level for other vegetables and potatoes is 0.1 mg/kg.

Desmetryne (Desmetryn, Semeron)

The active ingredient is 2-isopropylamino-4-methylamino-6-methylthio-1,3,5-triazine:



In the pure form, it is a white crystalline solid with a yellowish tint melting at 84-86 °C; its solubility in water is 580 mg/litre at 20 °C, it dissolves in ethanol and chloroform. It is marketed in the form of wettable powders containing 25 and 50% of the active ingredient.

Desmetryne penetrates into plants via their roots and leaves, consequently it may be applied over vegetating weeds. It is a good killer of fat hen, common chickweed, hempnettle, and bushy knotweed, preferably in the early stages of growth.

The weeds resistant to desmetryne include cabbage and meadow grass weeds, black bindweed, knotgrass, and scentless mayweed.

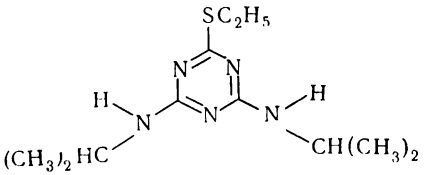
Desmetryne is recommended for killing weeds on fields of white and Jersey cabbage by spraying in one or two weeks after planting the seedlings (after their taking root) on seed plantations, or in the stage of 3-5 leaves of the crop. The rate of use of the 25% wettable powder is 1.6-2.4 kg (0.4-0.6 kg a.i.) per hectare, and of the 50% wettable powder is 0.8-1.2 kg/ha. The application of desmetryne in combination with inter-row cultivations makes it possible to do without manual weeding of the cabbage and thus to reduce the expenditure of labour needed to care for the crop by 18-25 man-days per hectare.

Spraying over dew lowers the effectiveness of desmetryne; rainfall on the next day after treatment also diminishes its action on the weeds. It is not recommended to apply desmetryne upon large harm by cabbage maggots. Desmetryne decomposes in the soil during six weeks.

Desmetryne has a low toxicity to humans and warm-blooded animals (see Table 29). The tolerance level in cabbage is 1 mg/kg.

Dipropetryne (Cotofor, Sancap)

The active ingredient is 2-ethylthio-4,6-di(isopropylamino)-1,3,5-triazine:



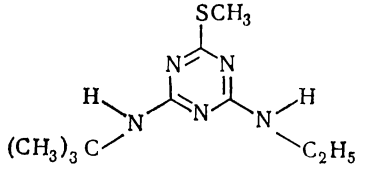
It is a white powder melting at 104-106 °C, poorly soluble in water (16 mg/litre at room temperature) and well in organic solvents.

For practical application, it is marketed in the form of an 80% wettable powder. It is a soil herbicide and is good for controlling the emergence of many mono- and dicotyledonous annual and biennial weeds. It is recommended for pilot application on cotton fields for spraying the soil prior to planting, when planting, or before emergence of the crop at a rate of 1.2-3.7 kg of the formulation (1-3 kg a.i.) per hectare.

Dipropetryne is moderately toxic to humans and warm-blooded animals (LD_{50} for rats is 390-420 mg/kg).

Terbutryne (Igran, Prebane)

The active ingredient is 2-ethylamino-4-tert-butylamino-6-methylthio-1,3,5-triazine:



It is a white powder melting at 104-105 °C, poorly soluble in water (58 mg/litre at 20 °C) and readily in organic solvents. It is a soil herbicide and a good killer of mono- and dicotyledonous annual and biennial weeds.

It is marketed in the form of a 50% wettable powder.

It is recommended for application on lavender plantations by spraying in the spring before the plants sprout at a rate of 6-8 kg of the formulation (3-4 kg a.i.) per hectare.

Terbutryne has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 2400-2980 mg/kg).

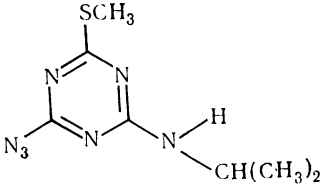
Polytriazine

This is a combined formulation consisting of a mixture of atrazine (24%), simazine (9%), and propazine (9%), the sum of the active ingredients being 50%. It is marketed in the form of a wettable powder. It kills the same weeds as the other triazine herbicides do. It is recommended for pilot application on corn fields by preplanting or preemergence spraying at a rate of 3-6 kg (1.5-3 kg a.i.) per hectare.

It has a low toxicity to humans and warm-blooded animals.

Aziprotryne (Mesoranil, Brasoran)

The active ingredient is 2-azido-4-isopropylamino-6-methylthio-1,3,5-triazine:



It is a colourless odourless crystalline powder melting at 95 °C. It dissolves poorly in water (55 mg/litre at 20 °C) and better in organic solvents such as acetone, toluene, and chloroform.

It is marketed in the form of a 50% wettable powder.

Aziprotryne is stable in storage and in the soil. As a result of its slight solubility in water, it is slowly washed out into the deeper layers of the soil. It persists for a longer time in weakly humus-enriched soil, but decomposes relatively more rapidly in soils rich in humus. As a result of its longer persistence in the soil (up to 115 days), it may harm sensitive crops.

It penetrates into plants through their roots and in insignificant amounts through their leaves, therefore it is incorporated into the soil before sowing or setting out the seedlings.

The herbicide is phytotoxic to many annual and biennial weeds including amaranth, barnyard grass, bristle grass, charlock, common chickweed, common spurrey, fat hen, field pennycress, knotweed, ragweed, and shepard's purse.

Cleavers, common fumitory, hempnettle, and wild radish are resistant to aziprotryne. It acts better on weeds in their early stages, up to 3-4 leaves. It does not kill perennial weeds with a deep root system. Aziprotryne accumulates in the soil in the top 5-centimetre layer and decomposes during 2.5-3 months.

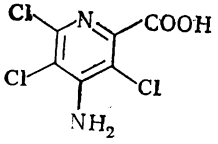
Aziprotryne is recommended for pilot use on white cabbage by spraying the soil before sowing or before setting out the seedlings at a rate of 3-10 kg of the formulation (1.5-5 kg a.i.) per hectare. No residues of aziprotryne are detected in cabbage when the rates of use and the periods of application are observed.

Aziprotryne has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 5833 mg/kg).

8.5.9. Heterocyclic Compounds

Picloram (Tordon, Amdon)

The active ingredient is 4-amino-3,5,6-trichloropicolinic acid:



It is a colourless crystalline substance melting at 215 °C (with decomposition). It dissolves poorly in water (430 mg/litre at 25 °C), and better in acetone (20 g/litre) and ethanol (10 g/litre). The amine and potassium salts of this acid dissolve well in water.

A variety of picloram formulations are manufactured for use as herbicides.

Tordon 22K is an aqueous solution of the potassium salt containing 25% of the active ingredient.

Tordon 101 is a mixture of amine salts of picloram (10.2%) and 2,4-D (39.8%), the content of the active ingredient being 50%.

Picloram penetrates into plants both via their roots and via their leaves, and is translocated well in them along the xylem and the phloem. When applied to the leaves, the rate of translocation increases with elevation of the temperature and a growth in the humidity, and lowers in dry and hot weather.

Many investigators have noted that picloram when applied to leaves is excreted by the roots of plants in an unchanged form.

Picloram is absorbed poorly by the colloids in the soil and may be washed out by the water of rainfall to a depth up to 1.5 m; the rate and depth of migration grow in soils with a lower content of organic matter. Picloram decomposes slowly in the soil and in plants. When incorporated into the soil in doses of 3-5 kg a.i./ha, it persists in it up to 3-7 years.

Shoots and young plants are more sensitive to picloram. It causes the leaves and stems to curl and perish. An increase in the concentra-

tion of picloram in plants is observed at the centres of increased metabolic activity.

In plants treated with picloram, the absorption of CO_2 decreases, and the flow of the assimilators from the leaves to the roots slows down.

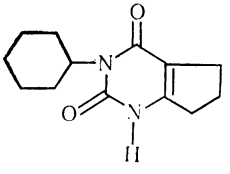
Picloram is a non-selective herbicide and is recommended for killing persistent offset weeds on uncultivated lands and at seats of Russian knapweed, and also for killing shrubs that propagate by root sprouting. The rate of use of picloram and tordon 22K is 4-8 kg (1-2 kg a.i.) and of tordon 101 is 4-7 kg (2-3.5 kg a.i.) per hectare.

The toxic residues of picloram in the soil may harm following crops in the crop rotation.

Picloram has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 3750 mg/kg, and for mice is 1500 mg/kg).

Lenacil (Venzar)

The active ingredient is 3-cyclohexyl-5,6-trimethyleneuracil:



The pure substance is a white odourless solid melting at 315.6-316.8 °C. It dissolves poorly in water (6 mg/litre at 25 °C) and well in pyridine. It is stable in storage, but decomposes under the action of alkalies.

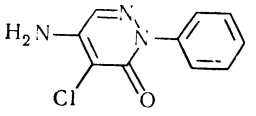
It is marketed in the form of an 80% wettable powder. It is a good killer of fat hen, wild radish, shepard's purse, mustard, common spurrey, common chickweed, bristle grass, barnyard grass, etc. Wild oats, amaranth, and all the perennial weeds are resistant to lenacil. The herbicide acts better on weeds when the soil contains sufficient moisture. It is recommended for killing weeds on sugar and table beet fields by spraying the soil before planting, when planting, and after planting before emergence of the crop at a rate of 1-2 kg (0.8-1.6 kg a.i.) per hectare.

Lenacil is used on strawberries for spraying the soil before emergence of the weeds at a rate of 2.5-5 kg (2-4 kg a.i.) per hectare.

Lenacil has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 10 000 mg/kg).

Pyrazon (Chloridazon, Pyramin)

The active ingredient is 5-amino-4-chloro-2-phenylpyridazin-3-one:



It is a pale yellow odourless crystalline solid poorly soluble in water (400 mg/litre at 20 °C), and soluble in acetone, methanol, and dimethylsulphoxide. It melts at 207 °C (decomposes).

Pyrazon is stable at ordinary temperatures. In the soil, it decomposes under the influence of microorganisms with the detachment of a benzene ring to form a 5-amino-4-chloro-pyridazin-3-one compound having no herbicidal properties. Pyrazon is inactivated in the soil during one vegetation period.

It is marketed in the form of a 60% wettable powder. It is recommended for killing weeds on fields of fodder, table, and sugar beets. The latter are resistant to pyrazon up to the stage of two leaves, therefore it is recommended to apply the formulation before emergence and over the seedlings of the beets, but at a temperature above 25 °C the plants may be harmed. The herbicide kills fat hen, wild radish, charlock, knotweed, etc. It has a poor effect on meadow grass weeds and perennial dicotyledonous ones such as sowthistle and field bindweed.

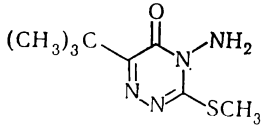
Pyrazon is used for killing weeds on sugar beet fields by spraying the soil before planting or before emergence of the crop at a rate of 4-8 kg (2.4-4.8 kg a.i.) per hectare, on red clover fields (a non-cover crop) by preplanting spraying of the soil at a rate of 4-5 kg (2.4-3 kg a.i.) per hectare.

Pyrazon inhibits photosynthesis in the plants sensitive to it, the content of chlorophyll "a" diminishing. Nitrogen metabolism is also disrupted, the nitrogen content in the roots decreasing, and in the green parts increasing. Phenol metabolism is also disrupted.

Pyrazon has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 3500 mg/kg).

Metribuzin (Lexone, Sencor, Sencorex)

The active ingredient is 4-amino-6-tert-butyl-3-methylthio-1,2,4-triazin-5-one:



It forms colourless crystals melting at 125.5-126.5 °C, poorly soluble in water (1.2 g/litre at 20 °C) and soluble in ethanol and acetone, better in methanol.

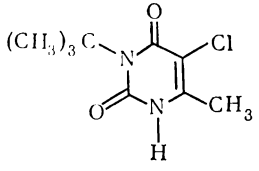
Metribuzin is available in the form of a 70% wettable powder. When incorporated into the soil, it kills many annual and biennial weeds such as ragweed, common fumitory, wild oats, barnyard grass, cleavers, shepard's purse, and bristle grass.

It is recommended for pilot application on tomato plantations (in the open soil) by spraying the soil before planting or setting out the seedlings at a rate of 1.1-1.4 kg (0.75-1 kg a.i.) per hectare.

Metribuzin has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 2000 mg/kg).

Terbacil (Sinbar)

The active ingredient is 3-tert-butyl-5-chloro-6-methyluracil:



It is a white crystalline odourless solid melting at 175-177 °C. It dissolves poorly in water (710 mg/litre at 25 °C) and moderately in xylene, dimethylsulphoxide, and cyclohexanone.

Terbacil is marketed in the form of an 80% wettable powder. It is a good killer of many annual and biennial di- and monocotyledonous weeds, and also acts on perennial ones.

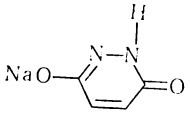
Terbacil is recommended for pilot application to kill weeds in citrus orchards (tangerines, lemons, oranges) by the directed spraying of the soil before the emergence of the weeds at a rate of 2.5-5 kg (2-4 kg a.i.) per hectare.

It may also be used in pip and stone fruit orchards (apples, pears, apricots, peaches, plums) by directed spraying at a rate of 1.9-5 kg (1.5-4 kg a.i.) per hectare.

Terbacil has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is 5000-7500 mg/kg).

MH-Sodium (MG-Sodium)

The active ingredient is the sodium salt of maleic hydrazide:



It is marketed in the form of a crystalline or yellowish powder containing 60% of the active ingredient. It is intended for controlling broomrape on watermelon fields. According to data of the All-Union Research Institute of Irrigated Agriculture and Melon Production, two- or three-fold spraying of watermelons with the formulation at a rate of 5.7 kg (3.4 kg a.i.) per hectare eradicates broomrape from watermelon fields during the entire vegetation period.

The harvest time when using this herbicide is 20 days.

MH-sodium is used on tomatoes by three-fold application against broomrape at a rate of 1 kg (0.6 kg a.i.) per hectare.

MH-sodium has a low toxicity to humans and warm-blooded animals.

8.5.10. Herbicide Mixtures (Combined Formulations)

Different herbicides owing to their definite selectivity can kill a limited number of weed species. For example, the derivatives of 2,4-D and MCPA kill many weeds from the class of dicotyledonous ones, but do not eradicate meadow grass weeds, while among the dicotyledonous plants they have only a slight effect on such widespread weeds as bushy knotweed, black bindweed, common spurrey, common chickweed, cleavers, and scentless mayweed. As a result, upon the prolonged application of these herbicides in the crop rotation, the amount of meadow grass and other weeds resistant to these herbicides grows. At the same time, there are herbicides that are good against weeds resisting derivatives of 2,4-D and MCPA. For instance, dicamba is a good killer of knotweed, scentless mayweed, and common chickweed.

Derivatives of 1,3,5-triazines are good against both mono- and dicotyledonous annual and biennial weeds, but only slightly affect perennial ones such as Canadian thistle, field bindweed, and Russian knapweed.

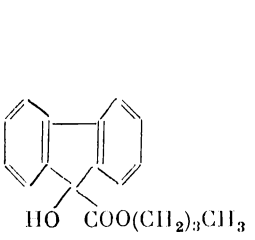
The use of combined herbicidal formulations makes it possible to eliminate the drawbacks of individual herbicides and substantially expand the number of species of weeds controlled.

Combined herbicides are produced mainly for extending the spectrum of their action, killing a larger number of weed species, and elim-

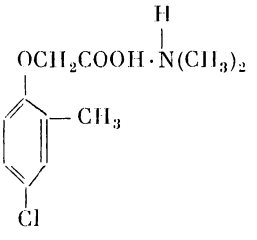
inating the repeated spraying of crops. The large family of combined herbicides includes actril AS and actril M, diamet-D, dialen, cambilene, biyalan, diapren, isolin, agelon, lumeton, and many other formulations.

Aniten C

The active ingredients are the butyl ester of 9-hydroxyfluorene-9-carboxylic acid (flurecol-*n*-butylester) (100 g/litre) and MCPA in the form of its dimethylamine salt (337 g/litre):



Flurecol-*n*-butylester



MCPA dimethylamine salt

Flurecol-*n*-butylester is a white crystalline solid melting at 71 °C, poorly soluble in water (36.5 mg/litre at 20 °C) and soluble in acetone, benzene, and ethanol.

It has a low toxicity to humans and warm-blooded animals (LD_{50} for rats is more than 5000 mg/kg).

Aniten C is marketed in the form of a 44% aqueous solution. It is recommended for pilot application for spraying spring wheat and barley in the tillering stage at a rate of 2-3 kg (0.9-1.3 kg a.i.) per hectare.

Aniten M

The active ingredients are flurecol-*n*-butylester (79 g/litre) and MCPA in the form of the isooctyl ester (251 g/litre).

Aniten M is available in the form of an emulsifiable concentrate containing 33% of the active ingredients and is recommended for pilot application against weeds on fields of spring wheat and barley at a rate of 2-3 kg (0.7-1 kg a.i.) per hectare.

The harvest time is 45 days.

Banlen

Banlen is a mixture of MCPA and dicamba in the form of the dimethylamine salt, the content of the active ingredients in an aqueous solution is 27%. It is a selective herbicide used to kill weeds

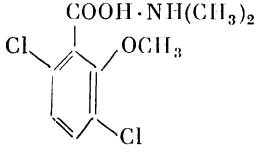
that are resistant to 2,4-D and MCPA. Cereal crops should be sprayed in the stage of the beginning of tillering before leaf tube formation.

It is recommended for killing weeds resistant to 2,4-D and MCPA on fields of wheat, rye, barley, and oats by spraying in the tillering stage of the cultivated plants at a rate of 4-8 kg (1.1-2.2 kg a.i.) per hectare.

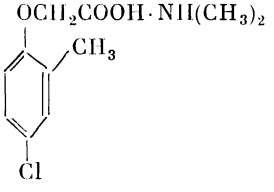
Banlen is moderable toxic to humans and warm-blooded animals.

Diamet-D

This is a combined formulation with systemic action consisting of the dimethylamine salt of 2-methoxy-3,6-dichlorobenzoic acid (2.7%):



and the dimethylamine salt of 2-methyl-4-chlorophenoxyacetic acid (41.9%):

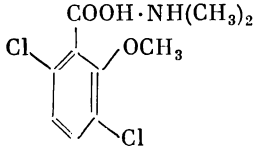


Diamet-D is a dark brown aqueous solution with a density of 1.16 g/cm^3 containing 44.6% of the active ingredients. As a combined systemic herbicide, it is recommended for killing weeds resistant to 2,4-D and MCPA on fields of cereal crops by spraying in the tillering stage at a rate of 2.5-3.9 kg (1.1-1.75 kg a.i.) per hectare.

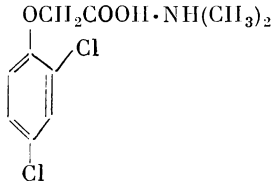
Diamet-D has a low toxicity to humans and warm-blooded animals.

Dialen

Dialen is a combined systemic herbicide. The active ingredient contains 3.6% of an aqueous solution of the dimethylamine salt of 2-methoxy-3,6-dichlorobenzoic acid



and 36.1% of the dimethylamine salt of 2,4-dichlorophenoxyacetic acid:



It is a brown liquid containing 40% of the active ingredient. The formulation penetrates well into plants through their roots and leaves. It kills many dicotyledonous weeds.

Dialen is recommended for spraying spring wheat, barley, and oats in the tillering stage at a rate of 1.75-2.25 kg (0.7-0.9 kg a.i.) per hectare for killing weeds resistant to 2,4-D and MCPA.

Dialen is moderately toxic to humans and warm-blooded animals.

Diapren

This is a combined formulation consisting of two herbicides: dicamba and mecaprop. It is marketed in the form of a 40% aqueous solution. It penetrates into plants via their leaves and roots. It is recommended for killing weeds resistant to 2,4-D and MCPA on spring wheat and barley fields by spraying in the tillering stage at a rate of 2.5-3.75 kg (1-1.5 kg a.i.) per hectare and for the spring spraying of winter wheat and rye fields at a rate of 3-5 kg (1.2-2 kg a.i.) per hectare.

It has a low toxicity to humans and warm-blooded animals.

Cambilene

Cambilene is a combination of four herbicides: mecaprop (150 g/litre), MCPA (100 g/litre), 2,3,6-TBA (25 g/litre) and dicamba (18.75 g/litre).

It is available in the form of an aqueous solution containing 29.4% of the active ingredient (294 g/litre). It is recommended for killing weeds resistant to 2,4-D and MCPA such as scentless mayweed, cleavers, common chickweed, spurrey, and perennial weeds on fields with cereal crops.

The pilot use of cambilene is recommended on wheat, barley, and rye by spraying with the solution in the tillering stage at a rate of 4-6 kg (1.2-1.8 kg a.i.) per hectare.

Cambilene is moderately toxic to humans and warm-blooded animals.

Lumeton

This herbicide is a combination of simazine (4.3%), mecaprop (24%), and methoprotryne (5%).

Methoprotryne (gesaran) is the common name of 2-isopropylamino-4-(3-methoxypropylamino)-6-methylthio-1,3,5-triazine.

Chemically pure methoprotryne is a colourless crystalline powder melting at 68-70 °C. It dissolves poorly in water (320 mg/l at 90 °C), but well in organic solvents. It is stable in the dry state and in aqueous suspension. In an alkaline or acid medium and at elevated temperatures it hydrolyzes with replacement of the methylthio group ($-OSH_3$) by a hydroxy group ($-OH$) in the second position.

When methoprotryne is used on cereal crops in the recommended doses, there are no problems with respect to residual amounts of it in the grain. Good results are obtained in weed killing when methoprotryne is combined with other herbicides.

Lumeton is marketed in the form of a 43% wettable powder. It is recommended for the pilot treatment of cereal crops against annual and biennial dicotyledonous and gramineous weeds. Lumeton penetrates into plants through their roots and leaves, hence it acts on sprouting and vegetating weeds. It persists in the soil during 6-8 weeks, therefore it may be used in crop rotation. It is used to spray spring wheat, barley, and oats in the stage of 2-3 leaves and in the tillering stage at a rate of 1.6-2.3 kg (0.7-1 kg a.i.) per hectare.

Lumeton has a low toxicity to humans and warm-blooded animals.

SIS 67 MEV

The active ingredients are MCPA (25%) and mecaprop (50%). It is marketed in the form of a water-soluble powder containing 75% of the active ingredients.

The formulation is intended for controlling annual dicotyledonous weeds (on fields of red clover) by spraying in the stage of 1-3 ternate leaves of the crop at a rate of 1.5-2 kg (1.1-1.5 kg a.i.) per hectare.

When the herbicide is applied in this way, from 75 to 80% of the dicotyledonous annual weeds are killed.

Biyalan

This combined formulation includes two herbicides—propanil and molinate. It is available in the form of a 60% emulsifiable concentrate. It is recommended for pilot use on spring wheat fields for killing mono- and dicotyledonous annual and biennial weeds by spraying in the stage of two-three leaves at a rate of 4 kg (2.4 kg a.i.) per hectare.

It is moderately toxic to humans and warm-blooded animals.

Isolin

Isolin is a combination of chlorpropham and linuron in the ratio of 1 : 1. It is marketed in the form of an emulsifiable concentrate containing 40% of the active ingredients. It is recommended for pilot use on carrot, onion, and bulb onion fields by preemergence spraying of the soil at a rate of 5-7.5 kg (2-3 kg a.i.) per hectare, and also on soybean fields at a rate of 10-15 kg (4-6 kg a.i.) per hectare.

Isolin has a low toxicity to humans and warm-blooded animals.

Camparol

This combined herbicide consists of simazine (15%) and prometryne (40%). It is available in the form of a 55% wettable powder.

It is recommended for killing annual and biennial weeds on potato fields by preemergence spraying at a rate of 3.6-5.5 kg (1.98-3 kg a.i.) per hectare.

It is prohibited to sell the potatoes until three months have elapsed after treatment. Camparol has a low toxicity to humans and warm-blooded animals.

Agelon

Agelon is a mixture of two herbicides—atrazine and prometryne. It is produced in the form of a 50% wettable powder. It is recommended for killing weeds on corn fields by preplanting spraying of the soil (with incorporation into the soil) before planting, when planting, or before emergence of the crop at a rate of 4-6 kg (2-3 kg a.i.) per hectare. Agelon has a low toxicity to humans and warm-blooded animals.

Acetlur

This herbicide mixture of TCA and lenacil is marketed in the form of an 86% wettable powder from white to light gray in colour. Acetlur kills annual and biennial mono- and dicotyledonous weeds and is recommended for spraying the soil before planting, when planting, or before the emergence of sugar, table, and fodder beets. The rate of use is 9.3-13.95 kg (8-12 kg a.i.) per hectare. It has a low toxicity to humans and warm-blooded animals.

Dalur

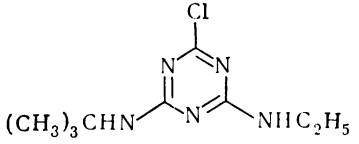
Dalur is a combination of lenacil and dalapon in the ratio of 1 : 4. It is marketed in the form of an 84% wettable powder.

It is recommended for weed killing on fields of sugar, table, and fodder beets by preplanting or preemergence spraying of the soil at a rate of 3.5-6 kg (3-5 kg a.i.) per hectare.

Dalur has a low toxicity to humans and warm-blooded animals.

Topogard

This combined formulation consists of 35% of 2-ethyl-amino-4-tert-butylamino-6-methylthio-1,3,5-triazine (terbutryne) and 15% of 2-ethylamino-4-tert-butylamino-6-chloro-1,3,5-triazine:



The first component of the mixture is an odourless crystalline powder poorly soluble in water, but well soluble in organic solvents. It is stable in the dry form and in aqueous suspensions, hydrolyzes at elevated temperatures and in an alkaline medium to 2-ethylamino-4-tert-butylamino-6-hydroxy-1,3,5-triazine.

Topogard is available in the form of a 50% wettable powder.

It is recommended for pilot application on potato plantations by preemergence spraying of the soil at a rate of 2-4 kg (1-2 kg a.i.) per hectare

It is prohibited to sell the potatoes until three months have elapsed after application of the herbicide. Topogard has a low toxicity to humans and warm-blooded animals.

Cartex M

The herbicides forming this mixture are propachlor (40%), monolinuron (13%) and prometryne (7%); the sum of the active ingredients is 60%. It is available in the form of a wettable powder and is recommended for killing weeds on sunflower fields by preemergence spraying of the soil at a rate of 5-8.3 kg (3-5 kg a.i.) per hectare.

8.5.11. Tank Mixes of Herbicides

Recent years have seen the widespread introduction of mixtures of herbicides prepared immediately before use. They have been named **tank mixes**. These mixes are formed depending on the specific composition of the weeds directly for a concrete field; here the doses may be varied depending on the crops and the sensitivity or resist-

ance of the weeds. Herbicides may be mixed with mineral fertilizers, insecticides, or fungicides. The joint application of herbicides with fertilizers improves the effectiveness of both the herbicides and the fertilizers, especially in the spring top-dressing of winter cereal crops.

The following tank mixes are recommended at present.

On winter wheat fields in the spring in the tillering stage, it is good to use the amine salt of 2,4-D (0.4 kg a.i./ha) and urea (30 kg a.i./ha) or the fertilizer "plav" (31% nitrogen) in an amount of 80 litres of the technical product (24.8 litres a.i.) per hectare.

Several herbicide mixtures are recommended for use on sugar beet fields.

In the regions of the Lithuanian SSR, Latvian SSR, Estonian SSR, Byelorussian SSR and in the western regions of the Ukrainian SSR, it is recommended to use a mixture of lenacil and TCA by spraying the soil before planting beets with a dose of 1.5 kg of an 80% formulation (1.2 kg a.i.) of the first component and 7 kg of a 90% formulation (6.1 kg a.i.) of the second component. This mixture is also recommended in the central and northern regions of the Ukrainian SSR, in the Moldavian SSR, the central regions of the chernozem zone of the RSFSR and in the Northern Caucasus, but the rate of use of the lenacil is increased to 2 kg of the formulation (1.6 kg a.i.) per hectare.

In the Latvian, Lithuanian, Estonian, Moldavian, and Byelorussian union republics, in the central regions of the Ukrainian SSR, the central regions of the chernozem zone of the RSFSR and in the Northern Caucasus, it is recommended to use a mixture of pyrazon and TCA for spraying the soil before planting sugar beets (pyrazon in an amount of 5 kg, or 3 kg a.i., and TCA in an amount of 7 kg, or 6 kg a.i. per hectare). In the irrigated conditions of the Kirghiz and Kazakh republics, the rate of use of the TCA formulation in this mixture is increased to 10 kg (8.7 kg a.i.) per hectare.

In the Moldavian SSR and the central regions of the Ukrainian SSR, it is recommended to use a mixture of pyrazon and cycloate at a rate of 5 + 5.3 kg (3 + 3.8 kg a.i.) per hectare, also for preplanting spraying of the soil.

Herbicide mixtures are also recommended on potato fields. Such a mixture, consisting of linuron and TCA with rates of use of 3-4 and 6.9 kg of the formulation (1.5-2 and 6 kg a.i.) per hectare, is applied by spraying the soil during 3-4 days after planting (on light-textured soils). On heavy-textured soils, the rate of use of the TCA is increased to 9.2 kg (8 kg a.i.) without increasing the amount of linuron.

Good results in killing weeds on potato fields are obtained by introducing a mixture of prometryne and TCA at a rate of 3-4 and 6.9 kg (1.5-2 and 6 kg a.i.) per hectare on light-textured soils; on heavy-textured soils the amount of TCA is increased to 8 kg a.i. This mixture is applied in the same periods as the preceding one.

Whenever herbicides are used on potatoes, the latter must never be sold until three months have elapsed after treatment.

On corn fields contaminated with Russian knapweed and other offset perennial weeds, it is recommended to use a mixture of 2,3,6-TBA (a 45% water-soluble concentrate) and an amine salt of 2,4-D at rates of 5-5.6 kg (2-2.6 kg a.i.) of the 2,3,6-TBA and 2.5 kg (1 kg a.i.) of the amine salt. The corn may be sprayed in the stage of 3-5 leaves.

The use of tank mixtures considerably expands the spectrum of action of herbicides and their effectiveness.

Chapter 9

DEFOLIANTS, DESICCANTS, AND RETARDANTS

9.1. Defoliants and Desiccants

Defoliants are substances causing the leaves of plants to fall. Desiccants are substances accelerating the drying of plants or their parts. Defoliants and desiccants find the greatest use in cotton growing because the machine harvesting of cotton is possible only after defoliation and desiccation.

As a result of chemical defoliation, the leaves fall in 4 to 15 days after treatment. This is attended by speeding up of the ripening and opening of the bolls, ripening of the seeds, an increase in the yield of the highest grades of raw cotton by 4-5%, and harvesting of up to 90% of the cotton before frosts set in. The quality of the fibres, and the biological and sowing properties of the seeds are not impaired by defoliation.

Such action of defoliants is explained by the fact that at the end of vegetation of cotton, the use of chemicals in the stage of ripening and opening of the bolls does not conflict with the biology of the plants. In this period, the formation of seed elements stops in plants, the growth of the stem retards, virtually no nutrient substances are used, the accumulation of dry matter stops, and the process of natural falling of the leaves begins. Defoliants appreciably accelerate this process because they stimulate the formation of an abscission layer in the leaf stalks.

Defoliation is commenced when one or two bolls open on most plants, while in more southern regions, when the large-scale opening of two to four bolls occurs.

Desiccation (the preharvest drying of standing plants) is recommended, in addition to cotton, on grass planted for seeds, on plantations of sugar beets, sunflowers, castor-beans, lupine, rice, hemp, etc. Desiccation accelerates the ripening of seeds and fruits, and

reduces their moisture content. This allows the harvesting and processing of the seeds to be mechanized and prevents their spoilage in storage.

Desiccation is especially helpful in conditions of unfavourable autumn weather, upon prolonged rainfall, and also when large amounts of fertilizers have been used and with irrigation, when the vegetation periods may become extended.

Desiccation is used as a way of drying standing plants after the formation of the crop, when it can have no negative influence on the magnitude and quality of the yield. A variety of substances can be used as desiccants, but most often magnesium chlorate, calcium chlorate-chloride, butylcaptax, and diquat are recommended.

In the Northern Caucasus, the desiccation of castor-beans is practised because this plant vegetates for a long time in these regions (the repeated growth of shoots and leaves occurs), which hampers machine harvesting.

The defoliation and desiccation of cotton are interrelated procedures when preparing the crop for machine harvesting. They substantially speed up the rates of ripening and opening of the bolls, which occurs not only because of the positive influence of the defoliants and desiccants, but also because of the change in the microclimate of the shrubs, their thinning and as a result diminishing of the humidity of the air and the moisture content of the soil, and elevation of the temperature in the air layer adjoining the soil surface.

The combination of cotton defoliation and desiccation makes it possible to harvest the crop earlier and advance fall ploughing accordingly, which is essential for obtaining a high yield the next year.

Defoliants and desiccants have an insecticidal and acaricidal action, which reduces the population of sucking and mandibulate insects by the following spring.

The defoliants used at present include calcium cyanamide, magnesium chlorate, calcium chlorate-chloride, and butifos.

Calcium Cyanamide (Cyanamide, Nitrolime)

The chemical formula is $CaCN_2$. The technical product is a dark-gray, almost black dusty powder with an odour of acetone; it contains 50-55% of calcium cyanamide, 18.5-20% of cyanamide nitrogen, and 0.5-1.5% of mineral oil.

If wetted in storage, calcium cyanamide becomes clotted and is not fit for use as a defoliant. For a good effect of calcium cyanamide, it is essential that moisture be present on the leaves, therefore it is applied by dusting over the dew in the early morning hours, or when the dew appears in the evening. At a temperature of 17 °C

and below, and also in dry weather, calcium cyanamide does not act as a defoliant. Upon the good and timely treatment with calcium cyanamide, cotton leaves first become lighter in colour, then turn yellow, red, and fall in 10-18 days.

Investigations have shown that under the action of moisture, air, and dew on calcium cyanamide, calcium hydrogen cyanamide and calcium hydroxide are formed:

$$2CaCN_2 + 2H_2O = Ca(OH)_2 + Ca(HCN_2)_2$$

As a result of further hydrolysis of the calcium hydrogen cyanamide, free cyanamide is formed:

$$Ca(HCN_2)_2 + 2H_2O = Ca(OH)_2 + 2H_2CN_2$$

Free cyanamide is soluble in water and penetrates well into leaves, which causes them to fall.

On moist cotton leaves, free cyanamide is formed during one hour.

Cyanamide has a deep physiological action on green leaves. It forms insoluble salts with the heavy metals (iron, copper, zinc) and, consequently, decomposes the enzymes responsible for the regulation of photosynthesis, and decomposes chlorophyll and carotene. Upon an increase in its concentration, it inhibits the respiratory enzymes (catalase). This is attended by stopping of the synthesis of organic substances in the leaves and the decomposition of protein compounds. Some investigators consider that a defoliant causes the same qualitative changes to occur in green leaves as in their natural falling, but they proceed more intensively.

The time of dusting with calcium cyanamide (the opening of 1-4 bolls on 50-70% of the cotton plants) is 10 days before harvesting, the dust being used at a rate of 35-60 kg (6.7-11.4 kg a.i.) per hectare.

The treatment of cotton with calcium cyanamide in the optimal periods has no negative effect on the technological properties of the fibres.

An increase in the doses detracts from the quality of defoliation because in this case the leaves dry, but do not fall.

Calcium cyanamide is moderately toxic to warm-blooded animals (LD_{50} for white mice is 400 mg/kg), and has an irritative effect when it gets on the mucous membranes, into the respiratory tracts, and onto the skin. The harvest time for cotton is 10-15 days. The maximum tolerated concentration in the air of the working zone is 0.5 mg/m^3.

Magnesium Chlorate (Magron, MC Defoliant)

The chemical formula of the pure substance is $Mg(ClO_3)_2 \cdot 6H_2O$. The technical product is a hygroscopic powder well soluble in water, or light brown granules containing 58-62% of magnesium chlorate hexahydrate and 38-40% of chlorides.

Its aqueous solutions are used for defoliation and desiccation. Magnesium chlorate is effective at a mean daily temperature of 17-18 °C; when the temperature drops to 9-10 °C, the effectiveness of this substance as a defoliant does not diminish.

Magnesium chlorate is not a systemic defoliant and penetrates only into the leaves which it is applied to. Complete penetration of the substance occurs during one hour. Magnesium chlorate, unlike calcium cyanamide, functions well as a defoliant even in the absence of dew, and also at a low relative humidity of the air.

It is recommended to spray developing cotton with magnesium chlorate when an average of two bolls open on each shrub.

Magnesium chlorate causes sharp disruption of water conditions in cotton plant leaves, inhibits photosynthesis, decomposes chlorophyll and carotene, and disrupts carbohydrate and protein metabolism.

Hydrolytic processes predominate over synthesizing ones. Next the leaves wilt, an abscission layer forms at the base of their stalks, and they fall. Magnesium chlorate acts as a defoliant in comparatively small doses (7-35 kg/ha). The use of larger doses than the recommended ones may lead to desiccation of the leaves, but they will not fall.

Magnesium chlorate is widely employed not only as a defoliant, but also as a desiccant on many crops (cotton, rice, sunflowers, castor-beans, soybeans, sugar beet seed plantations, hemp, etc). The rates of use and the conditions of application of magnesium chlorate are given in Table 33.

Magnesium chlorate is moderately toxic to humans and warm-blooded animals (LD_{50} for mice is 620 mg/kg).

Calcium Chlorate-Chloride

It is a light gray liquid containing 30-32% of calcium chlorate $Ca(ClO_3)_2$ (the active ingredient) and 28-29% of calcium chloride $CaCl_2$. It is used in the form of an aqueous solution as a defoliant and desiccant.

It has the same physiological action on cotton leaves as magnesium chlorate (the active component of both formulations is the chlorate ion), but in identical doses (of the active ingredient) calcium chlorate-chloride acts more mildly, which manifests itself in the slower opening of the bolls.

Table 33. Application of Magnesium Chlorate for Defoliation and Desiccation

Crop	Rate of use, kg/ha		Conditions of use	Harvest time, days
	formulation	active ingredient		
Cotton	8-20	4.8-12	Spraying when 1-4 bolls open (defoliation)	6
Ditto	25-35	15-21	Spraying of plants when at least 50% of the bolls open (desiccation)	6
Rice	25-50	15-30	Spraying in period of complete ripeness of 70-75% of the caryopses (desiccation)	10
Wheat	20-30	12-18	Spraying of crop at the beginning of wax ripeness of grain (desiccation)	10
Sunflowers	20-30	12-18	Spraying when anthodia begin to turn brown (desiccation)	10
Potatoes	25-30	15-18	Spraying of plants upon completion of tuber formation and hardening of skin (desiccation)	10
Castor-beans	15-20	9-12	Spraying in period when pods on central raceme turn brown (desiccation)	10
Soybeans	20-30	12-18	Spraying when beans on the lower and middle storeys of the plants turn brown (desiccation)	10
Sugar beet seed plantations	15-30	9-18	Spraying of plants when 30-40% of seed bolls turn brown (desiccation)	10
Hemp	12-18	7.2-10.8	Spraying upon completion of blossoming of male racemes (desiccation)	10
Seed hemp	25-30	15-18	Spraying in period when seeds at the middle of a raceme ripen	10
Grapevines (technical strains)	15	9	Treatment against gray rot	30
Ditto	7	4.2	Preharvest defoliation	20
Seed plantations of radish	25-33	15-20	Spraying in period of wax ripeness with seed moisture content of 50-55%	10

Calcium chlorate-chloride is effective as a defoliant in cotton-growing regions with or without dew in various temperature conditions.

It is recommended for application on cotton as a defoliant by spraying at a rate of 20-30 kg (8.4-12.6 kg a.i.) per hectare in the period of opening of 1-4 bolls on most shrubs, and as a desiccant

when at least 50% of the bolls open at a rate of 40-50 kg (16.8-21kg a.i.) per hectare. Spraying in both cases must be terminated six days before harvesting the cotton.

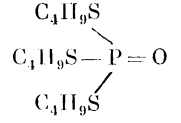
Calcium chlorate-chloride is used as a desiccant on fields of rice, sunflowers, and on sugar beet seed plantations at a rate of 40-50 kg (16.8-21 kg a.i.) per hectare. Its pilot use has been recommended at the same rate for the desiccation of potatoes, castor-beans, and soybeans.

In all cases, the harvest time is six days.

Calcium chlorate-chloride has a low toxicity to humans and warm-blooded animals (LD_{50} for mice is 1112 mg/kg). The tolerance level in the air of the working zone is 2.5 mg/m^3.

DEF (Butifos)

The active ingredient is S,S,S-tributylphosphorotrithioate:



It is marketed in the form of a light-brown emulsifiable concentrate containing 70% of the active ingredient and 30% of OP-7.

As a defoliant, it is characterized by a high activity in various conditions of growing cotton; better falling of the leaves occurs at 18-20 °C, while the action of DEF is inhibited when the temperature drops. Consequently, in such conditions its dose must be increased by 20-25%.

After the application of DEF, the leaves begin to fall in 3-5 days, and in 7 days the amount of fallen leaves may be 80-90%. If less of them fall, the treatment should be repeated. During the first three or four days after treatment with DEF, no falling of the leaves is observed, they remain green, the nutrient substances flow out of them into the bolls, and an abscission layer forms. On the fifth or sixth day, mass falling of the leaves begins.

DEF acts rapidly, but relates to mild defoliants because it does not damage the terminal bud. Hence, the repeated growth of leaves is possible.

It is recommended to begin treatment with DEF when 1-4 bolls open on a cotton shrub.

DEF relates to moderately toxic substances (LD_{50} for test animals is 177-300 mg/kg). The tolerance level in the air of the working zone is 0.2 mg/m^3.

The harvest time for DEF is 10 days.

DEF rapidly decomposes in leaves to form non-toxic metabolites.

The doses of DEF for treating cotton are 1.4-3 kg (0.98-2.1 kg a.i.) per hectare; in higher doses it may cause drying of the leaves without their falling.

The rates of use of magnesium chlorate, calcium chlorate-chloride, and DEF depend on the development of the cotton (Table 34).

Table 34. Rates of Use of Desiccant Depending on Development of Cotton (Recommendations of All-Union Research Institute of Cotton Growing for Month of September)

Formulations	Rate of use of formulation, kg/ha					
	Vigorous, greatly verdant plants			Moderately verdant plants with normal growth		
	Beginning of month	Middle of month	End of month	Beginning of month	Middle of month	End of month
Defoliants						
DEF	3	3	—	2	2.0-2.5	—
Magnesium chlorate	—	10-12	12-14	—	8-9	10-12
Calcium chlorate-chloride	—	24-25	28-30	—	20-22	24-25
Desiccants						
Magnesium chlorate	—	—	28-30	—	—	24-25
Calcium chlorate-chloride	—	—	48-50	—	—	42-45

The rate of use of the liquid in the aerial spraying of cotton with DEF, magnesium chlorate, or calcium chlorate-chloride is 100 litre/ha.

When employing tractor sprayers, the rate of use of the working liquid must be kept within 640-1200 litre/ha, depending on the height of the plants and the magnitude of the leaves' surface.

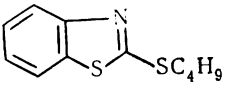
Diquat (Reglon)

Diquat is available in the form of a 20% aqueous solution. It is used for the desiccation of sugar beet seed plantations by spraying the plants in the period when 30-40% of the seed bolls turn brown at a rate of 5-10 kg (1-2 kg a.i.) per hectare with a harvest time of 10 days.

Its pilot application is allowed for desiccating alfalfa seed plantations by spraying not later than a week before harvesting in conditions of irrigated farming at a rate of 2-4 kg (0.4-0.8 kg a.i.) per hectare.

Butylcaptax

This is a combined defoliant, consisting of a 90% emulsifiable concentrate of butylcaptax (butyl-2-benzthiazolyl-sulphide):



and a 60% wettable powder of magnesium chlorate $Mg(ClO_3)_2 \cdot 6H_2O$.

Butylcaptax is recommended for pilot application in the defoliation of fine-staple cotton at a rate of 10 kg/ha. The cotton is sprayed when four or five bolls open with a harvest time of 10 days.

The formulation is moderately toxic to humans and warm-blooded animals. The maximum tolerated concentration of butylcaptax in the air of the working zone is 2 mg/m^3.

9.2. Retardants *

The first reports in the press on the ability of certain nicotine and other compounds to retard the growth of bean plants appeared at the end of the nineteen fourties. Later, several compounds were separated that are capable of affecting the habitus of plants without any appreciable disruptions of their important physiological functions. Among them are 2,4-DIS [N-2,4-dichlorobenzyl)-N-methyl-2-(3-pyridil) pyrrolidinium chloride], AMO-1618 (the methochloride-2-isopropyl-4-dimethylamino-5-methylphenyl ester of 1-piperidine-carboxylic acid), and chlorphonium [tributyl-2,4-(dichlorobenzyl) phosphonium chloride].

At the end of the fifties, the strong growth-retarding effect of 2-chloroethyltrimethylammonium chloride was noted, while in 1961 reports appeared on the prevention of the lodging of wheat on rich soils with the aid of this formulation, given the common name of chlormequat chloride or chlorcholine chloride.

At present, substances known as **retardants**, a class of plant growth regulators, are widely used in agriculture to control the growth of plants.

Retardants are characterized by a low molecular mass, are readily soluble in water, and penetrate freely into plants. A common chemical property of most retardants is the presence in them of organic cations that play a major role in the processes of energy exchange in cells.

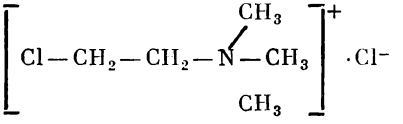
Chlormequat chloride has come into especially great favour for preventing the lodging of cereal crops.

* Section 9.2 was written by L. G. Gruzdyev, Cand. Sc. (Biology).

In the USSR, chlormequat chloride is used on cereal crops on an area of about 10 million hectares, in vegetable growing, and horticulture. Some other retardants are also used, as well as their combinations and mixtures with herbicides and fertilizers.

Chlormequat Chloride (Chlorcholine Chloride, CCC)

The active ingredient is 2-chloroethyltrimethylammonium chloride:



It is synthesized comparatively easily from trimethylamine and 1,2-dichloroethane:

$$N \equiv (CH_3)_3 + CH_2Cl - CH_2Cl \longrightarrow ClCH_2 - CH_2 - N^+ \equiv (CH_3)_3 \cdot Cl^-$$

Chlormequat chloride in the pure state is a white crystalline highly hygroscopic substance with a fish-like odour melting at 245 °C. Its molecular mass is 158.1 and its density is 1.14 g/cm³. It has a moderate toxicity (LD_{50} for rats is 600 mg/kg, and for mice is 400 mg/kg).

The formulation contains 70% of the active ingredient.

Chlormequat chloride has a growth regulating action on more than 80 species of plants and is widely used in agriculture to prevent the lodging of a number of cereal crops, in horticulture, floriculture, ornamental gardening, and vegetable growing.

The lodging of cereal crops leads to considerable losses of the yield, reaching 25-30%. The quality of the grain of lodged plants diminishes, the use of machinery is hampered, and its output decreases, which in the long run is associated with substantial additional costs.

The main causes of lodging are a high humidity of the air, abundant rainfall in summer, strong winds, and increased doses of mineral, especially nitrogen, fertilizers. Lodging is facilitated by excessively close growing of the plants, their insufficient lighting, shallow incorporation of the seeds, infection of the plants by diseases, harm by pests, the non-uniform introduction of fertilizers, and sometimes also the abundant development of weeds.

The main way of preventing lodging of cereal crops is to spray the plants with an aqueous solution of chlormequat chloride.

The optimal dose of the formulation in the treatment of crops is 2-4 kg a.i./ha.

Here account must be taken of the disposition of the agricultural crops and varieties being treated to lodging and of the conditions facilitating it listed above.

To treat plants with surface equipment, the hectare dose of the formulation is diluted in 50-200 litres of water depending on the type of sprayers used; for aerial spraying the same dose is diluted in 25-50 litres of water.

Spraying is performed in calm weather. If a rain falls in 2-2.5 hours after spraying, the action of the formulation becomes weaker. An important condition for the use of chlormequat chloride is spraying in good time. Cereal crops should be treated once in the spring in the stage of the end of tillering and the beginning of shooting (stages III-IV of organogenesis), when the plants reach a height of 15-25 cm. This is the time when differentiation of the ear proceeds, the activity of the meristem terminates in all the leaves except the last one, and the lower internodes of the stalk are formed. After treatment at this time, the lower internodes become shorter and thicker, as a result of which the strength of the straw and the resistance to lodging increase. Spraying at earlier periods when the ear's meristem has not yet become differentiated may lead to a decrease in the number of ears. Later spraying of the plants closer to the middle of ear formation results in shortening of only the upper internodes, and lodging of the plants is not always prevented.

The action of chlormequat chloride is based on inhibiting the division of the cells in the middle or subtop zone of the apical cone meristem from which the stalk is formed later. The formulation does not affect the top zone of the meristem from which the leaves and ears develop, or affects it considerably more weakly. Chlormequat chloride inhibits the growth of the cells of a young growing stalk and increases their division in a lateral direction. This is attended by an increase in the diameter of the stalk, greater development of the mechanical tissue facilitating the thickening of the shells of the cells, and an increase in the number of fibro-vascular bundles.

Such changes in the anatomic structure and morphology of the treated plants are associated with a harmonic readjustment of their entire metabolism: the activation of nitrogen exchange, an increase in the content and a change in the composition of the chlorophyll, an increase in the intensity of photosynthesis, and a certain inhibition of the synthesis of natural growth regulators with an increase in the content of natural stalk growth inhibitors and their activity.

The use of chlormequat chloride is most effective as a means of increasing the resistance to lodging on wheat and rye fields. When the maximum dose (4 kg/ha) is used on barley and oat fields, a restriction of stalk growth is observed in some varieties of these plants,

but as a whole the effectiveness of the formulation for them as a means of preventing lodging is appreciably lower than for wheat.

The reaction of different varieties of the same plant to treatment with chlormequat chloride is not the same. For long-stalk lodging varieties of wheat, the dose of chlormequat chloride must be larger than for short-stalk ones. The effectiveness of the formulation is also determined by the soil and climatic conditions and the quality of the agrotechnical measures. The best results are obtained when growing lodging varieties of wheat in conditions of an intensive system of farming on highly fertile soils, in years with a large amount of atmospheric precipitation, with irrigation and the use of large doses of nitrogen fertilizers.

Treatment with chlormequat chloride increases the resistance of cereal crops to a lack of water, a surplus of salts, low and high temperatures, and to certain diseases.

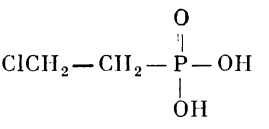
The results of numerous investigations performed in the USSR and in other countries showed that chlormequat chloride has no negative effect on the quality of the yield. The substance itself completely decomposes in a plant in 2.5-3 weeks after application. No changes occur in the grains in the content of proteins and gluten and in the quality of the gluten. The combined use of large doses of nitrogen fertilizers and chlormequat chloride made it possible to noticeably increase the protein content of the grain and its baking properties. The formulation does not substantially affect the fractional and amino acid composition of the grain proteins and the biological value of the grain. The sufficiently extended periods of application of chlormequat chloride in the spring allow the joint use of the retardant with herbicides such as 2,4-D, MCPA, mecoprop, and dicamba. In this case, the economical effectiveness of preventing lodging is summed with the effect of killing or suppressing weeds. It has been established by practice that chlormequat chloride does not react in a solution with any of the most favoured herbicides.

It is good practice to prepare a mixture of the substances immediately before use. The vessel used to prepare the mixture is filled up to half of its volume with water, and then the chlormequat chloride and herbicide are added. Such a mixture does not become turbid, forms no precipitate, and is well distributed over the surface of the plants. Upon the joint use of chlormequat chloride with certain herbicides, burning of the leaves may be observed. Investigations performed by the Central Institute for the Agrochemical Catering to Agriculture together with the Ivanovo Agricultural Institute have shown that when preparing mixtures it is desirable to lower the recommended dose of one of the formulations by 15-25%, which is not associated with a loss of effectiveness in the action of the components. The application of chlormequat chloride in

one solution with herbicides and a nitrogen fertilizer (up to 30 kg a.i./ha of urea) is also promising. Such solutions do not cause burning of the plants, intensify their metabolism, and increase the yield up to 25% in comparison with a control field, which for conditions of the central regions of the non-chernozem zone amounts to 0.5-1.1 more tonnes of grain per hectare. The addition to the same solution of microelement sulphates to a concentration of 0.1% did not lower the effectiveness of the mixture components and had no additional effect on the yield, but appreciably increased the content of the relevant microelements in the grain and the straw. This improved their food and fodder qualities. This procedure is especially effective on soils depleted of certain microelements.

Ethephon (Ethrel, Florel)

The active ingredient is (2-chloroethyl)phosphonic acid:



It is well soluble in water, methanol, and ethanol. It dissolves poorly in non-polar solvents such as benzene and toluene. Its melting point is 74.5 °C. It decomposes rapidly in an alkaline medium and liberates ethylene.

Ethephon has a low toxicity to humans and warm-blooded animals (LD_{50} with peroral ingestion is over 4200 mg/kg for rats).

Ethephon is the active ingredient of a number of retardants. It is used to prevent the lodging of cereals in a dose of 1.5-2 kg a.i./ha in a solution of 150-300 litres.

Its action on plants is similar to the influence of hormonal antiauxins. In cereals treated in the stem extension stage, the growth is retarded, the development of the mechanical tissues of the stalk increases, the lower internodes become shorter, and the plants become considerably more resistant to lodging, the action of strong storms, winds, and to other unfavourable conditions that usually cause the abundant lodging of crops. The action of ethephon leads to an increase in the yield of a number of cereal crops (barley, oats, rice, rye, wheat), leguminous and vegetable crops.

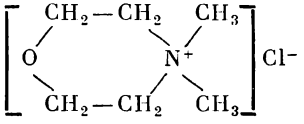
Ethephon has a polyfunctional action, affecting the nucleic and protein metabolism of plants.

According to data of the Belorussian and Latvian Research Institutes of Agriculture, and also of scientific institutions of the GDR, rye treated with ethephon did not lodge when nitrogen was incorporated into the soil at a rate of 100-140 kg/ha and more. The resistance to lodging in years with unfavourable weather conditions

increased twofold and more. The positive factors noted included shortening of the plants by 15-25%, an increase in the number of productive stalks, good grain forming, and more uniform ripening. This made it possible to gather from 0.3 to 0.9 tonne of grain additionally from each hectare. Tests showed that the use of ethephon on rye substantially reduced the cost of mechanized treatment and was indisputably an economically effective measure.

N,N-dimethylmorphinium Chloride

This substance has the following chemical formula:



It was synthesized in the FRG in the seventies. It has a strong retardant action on cereals such as wheat, oats, rice, and barley. It has passed numerous tests for preventing the lodging of barley, rice and oats on which the effectiveness of chlormequat chloride is low. The substance is not phytotoxic.

Chapter 10

THE COMBINED USE OF PESTICIDES

The combination of various chemical means of plant protection is widely employed in agriculture. Mixtures of pesticides are prepared and used to:

expand the spectrum of action of a pesticide to various species of harmful organisms;

increase the toxicity of a formulation with respect to harmful organisms;

prolong the duration of protective action of a pesticide;

lower the toxicity of a formulation to the plant being protected;

eliminate the adverse consequences of chemical treatments;

obtain the maximum economical effect from the use of pesticides.

Pesticides are combined most often to expand the spectrum of their action. Combined formulations include pesticides intended for application against objects either close or remote in their nature. Seed protectants such as mercurhexan whose composition includes ethylmercury chloride (fungicide and bactericide), hexachlorobenzene (fungicide), and HCH (insecticide) make it possible to protect seeds and shoots of cultivated plants against diseases and pests.

The combined herbicides banlen and cambilene, having a broader spectrum, are good killers of weeds resistant to 2,4-D and MCPA on cereal crop fields.

In plant protection practice, the periods of controlling various pests often coincide, therefore the joint treatment with several pesticides is practised. Mixtures of acaricides and organochlorine insecticides are used to kill insects and mites. A group of measures for protecting a garden may provide for combined treatments with insecticides to control codling moths and with fungicides to control diseases. The joint application of organophosphorus and organochlorine insecticides and herbicides (derivatives of 2,4-D) is possible on spring cereal crops for controlling weeds and diminishing the harm to plants by frit flies.

The reaction of the components of a pesticide mixture may increase the toxicity of one of them.

The mutual influence of the components of a mixture may be of an additive nature (the toxicity level of the mixture equals the sum of the levels of the individual components, i.e. $0.5LD_{50}$ of substance A + $0.5LD_{50}$ of substance B equal LD_{50} of the mixture A + B), synergetic (the toxicity level of the mixture is higher than the sum of the levels of the individual components, i.e. LD_{50} of the mixture A+B is larger than 0.5 LD_{50} of substance A + $0.5LD_{50}$ of substance B), or antagonistic (a phenomenon that is the opposite of synergism, when LD_{50} of the mixture A + B is smaller than $0.5LD_{50}$ of substance A + $0.5LD_{50}$ of substance B).

Antagonism is extremely undesirable when using mixtures of physiologically active substances.

The phenomenon of synergism is of the greatest significance for improving the effectiveness of chemical means of plant protection. A synergetic effect is exhibited in a pesticide mixture in the following cases.

1. When one of the components of the mixture facilitates the better penetration of a toxic substance into a harmful organism. The high effectiveness of the formulation trichlorol-5 against scales and wintering stages of other insects is due to the mineral oil in it facilitating the penetration of the trichlorometafos-3 under the scutellum of the San Jose scale or through the egg shells of insects.

This also underlies the use of herbicide oils with an addition of DNOC to kill vegetation.

2. When one substance prevents the rapid detoxification of an active component inside a harmful organism or in the soil. When a mixture of organophosphorus compounds enters the organism of an insect, one of them may greatly inhibit the activity of aliesterase, thus preventing the decomposition of the second substance. For example, a high synergetic effect in the inhibition of aliesterase has been revealed in a mixture of trichlorfon with dichlorvos.

Table 35. Compatibility of Selected Insecticides, Acaricides, and Fungicides

	Insecticides and acaricides																Fungicides							
	Carbaryl	Cyhexatin	Diazinon	Dichlorvos	Dicofol	Dinitro compounds	Endosulfan	Malathion	Metasystox	Oils	Phosalone	Phosmet	Polychlorocyclodienes	Tetradifon	Toxaphene	Benomyl	Captan, folpet	Copper formulations	Dinocap	Dodine	Quinomethionate	Wettable sulphur	Zineb, maneb
Insecticides and acaricides																							
Carbaryl	×	+	+	+	+	0[1]	+	+[7]	+	0	0[1]	+	+	+	+	+	+	0[11]	+	+	+	+	+
Cyhexatin	+	×	+	+	+	0[1]	+	+	+	+[12]	+	+	0[1]	+	+	+	+	+	+	0[1]	+	+	+	+
Diazinon	+	+	×	+	+	+	+	+	+	+	+	0[1]	+	+	+	+	+	0[9]	0[8]	+	+	+	+[10]
Dichlorvos	+	+	+	×	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Dicofol	+	+	+	+	×	+	+	+	+	+	+	+	+	+[4]	+	+	+[4]	+	+[4]	+	0[1]	+[6]	+
Dinitro compounds	0[1]	0[1]	+	+	+	×	0[1]	+	+	—	0[1]	+	+	+	+	0[1]	—	0[3]	—	0[1]	—	0[3]	+
Endosulfan	+	+	+	+	+	0[1]	×	+	+	+	+	+	+	+	+	+	+[4]	+	+	+	+	+	+
Malathion	+[7]	+	+	+	+	+	+	×	+	+	+	+	+	+	+	+	+[4]	+	+[4]	+[4]	+	+	+
Metasystox	+	+	+	+	+	+	+	+	×	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Oils	0	+[12]	+	+	+	—	+	+	+	×	+	+	+	+	0[1]	+[2]	—	+	—	+	—	0[3]	+
Phosalone	0[1]	+	+	+	+	0[1]	+	+	+	+	×	0[1]	+	+	+	+	+	+	+	—	0[1]	—	+
Phosmet	+	+	0[1]	+	+	+	+	+	+	+	0[1]	×	+	+	0[1]	+	+	0[1]	+[4]	+	+	+	+
Polychlorocyclodienes	0[1]	+	+	+	+	+	+	+	+	+	+	+	×	+	+	0[1]	+[4]	+	+[4]	+	+	+	+

Tetradifon	+	+	+	+	+[4]	+	+	+	+	+	+	+	+	×	+	0[1]	+	+	+[4]	+	0[1]	+	+
Toxaphene	+	+	+	+	+	+	+	+	+	0[1]	+	0[1]	+	+	×	0[1]	0[1]	+	+[4]	+	0[1]	+	+
Fungicides																							
Benomyl	+	+	+	+	+	0[1]	+	+	+	+[2]	+	+	0[1]	0[1]	0[1]	×	+	+	+	+	+	+	+
Captan (folpet)	+	+	+	+	+[4]	—	+[4]	+[4]	+	—	+	+	+[4]	+	0[1]	+	×	0[9]	+	+	+	+	+
Copper formulations	0[11]	+	0[9]	+	+	0[3]	+	+	+	+	+	0[1]	+	+	+	+	0[9]	×	0[1]	0[1]	0[1]	+	0[9]
Dinocap	+	+	0[8]	+	+[4]	—	+	+	+	—	+	+[4]	+[4]	+[4]	+[4]	+	+	0[1]	×	0[8]	0[1]	+	+
Dodine	+	0[1]	+	+	+	0[1]	+	+[4]	+	+	—	+	+	0[1]	+	+	+	0[1]	0[8]	×	+	+	+
Quinomethionate	+	+	+	+	0[1]	—	+	+	+	—	0[1]	+	+	0[1]	0[1]	+	+	0[1]	0[1]	+	×	—	+
Wettable sulphur	+	+	+	+	+[6]	0[3]	+	+	+	0[3]	—	+	+	+	+	+	+	+	+	+	—	×	+
Zineb, mancozeb	+	+	+[10]	+	+	+	+	+	+	+	+	+	+	+	+	+	+	0[9]	+	+	+	+	×

Symbols: + = compatible; 0 = may be incompatible (see footnote); − = incompatible.

Notes:
1. Not usually mixed together or compatibility unknown.
2. Addition of certain insecticides or fungicides may cause phytotoxicity in some crops.
3. Sensitive to adverse weather conditions.
4. Use wettable or soluble powder forms.
5. Mix only in equipment having excellent agitation; spray immediately upon mixing.
6. Do not apply dicofol within two weeks following sulphur spray or dust.
7. The combination of malathion with carbaryl may cause injury to cotton.
8. May cause injury to certain apple and pear varieties under some conditions.
9. When mixed with water, decomposes after standing.
10. Do not apply zineb in combination with diazinon on apricots.
11. Do not mix carbaryl with Bordeaux mixture or other alkaline solutions.
12. Do not use cyhexatin with oil on citrus, stone fruits, or almond.

3. When the toxicants of a mixture differing in their mechanism of action inhibit the same vitally important physiological reaction of an organism at different stages of it or different parallel reactions.

The combined application of pesticides in a number of cases increases the duration of plant protection against pests. For example, a mixture of malathion with tetradifon ensures the reliable protection of cucumber plants against the spider mite during 30-40 days.

Malathion has a low persistence and effectively eradicates adult mites and their larvae during 7-10 days, while tetradifon protects the plants from the appearance of the mites for a longer period.

Cuprosan (a mixture of copper oxychloride with zineb) burns plants to a smaller extent than copper oxychloride alone.

Dichloroacetamide, being itself a substance with a low biological activity, protects corn from harm by herbicides of the thiocarbamate group without lowering their effectiveness against weeds.

The use of mixtures of acaricides and organochlorine insecticides prevents the mass reproduction of phytophagous mites observed after application of only the latter. Mixtures of specific acaricides with organophosphorus compounds are an effective means for preventing the appearance of specific resistance in mites.

Finally, the combined use of pesticides makes it possible to substantially reduce the cost of treating agricultural crops and obtain cheaper products.

The combined use of pesticides, however, may sometimes lead to negative results. The toxicity of formulations lowers because of chemical reactions with the formation of non-toxic products. For example, in connection with the fact that organophosphorus compounds rapidly decompose in an alkaline medium, they must never be combined with Bordeaux mixture, lime, or lime sulphur. The period of the protective action of these insecticides diminishes simultaneously.

When desmetryne is used to kill cabbage weeds in combination with emulsifiable concentrates of insecticides, strong burning of the plants is observed.

The effectiveness of pesticides may lower because of the phenomenon of antagonism. This is possible when mixtures of pesticides are used having the same mechanism of action, but a different toxicity. In this case, the less active component may displace the more active one from the "battlefield" and lower the toxicity of the mixture.

The proper use of pesticide combinations increases their effectiveness, the productivity of labour in the performance of chemical treatments, and does away with some shortcomings of the chemical method of plant protection against pests, diseases, and weeds.

Numerous investigations and great practical experience have served as the basis for working out schemes of the compatability

of pesticides, one of which is presented in Table 35. It must be borne in mind that it is good to use a combination only when the periods of treatment with each of its components coincide. It must also be remembered that the stability of an active ingredient, which does not customarily change even in prolonged storage, may be harmed when formulations are mixed.

Chapter 11

BIOLOGICAL CONTROL

At present, chemical means of plant protection are being supplemented by biological control agents—pathogens of pest diseases: bacteria, viruses, fungi, microsporidia, and substances produced by them.

For the first time in world practice, experiments with entopathogenic microorganisms were run by I. Mechnikov and I. Krasilshchikov in 1908. The fungus *Metarrhizium anisopliae* (Metsh) was used to control beet weevils in large-scale field tests.

At the beginning of the 20th century, the investigations begun by Mechnikov were expanded and elaborated by academician V. Pospelov. He set out the most important theoretical propositions relating to the ways of using microorganisms for the biological control of agricultural pests. The leading role in them was relegated to ecological factors in the development of the epizooties of harmful insects. Great significance was attached to the influence of pathogenic microorganisms on the reduction of the fertility of pests. The participation of intestinal microflora in mass outbreaks of insect diseases was not only discovered, but was also given a leading role in the above process.

Active research made it possible to separate virulent strains of certain species of entomopathogenic bacteria found in nature that served as the basis for creating and testing the first specimens of biological control agents.

By the end of the fifties, the bacterial agent entobacterin 3 was produced, and in 1962 it was recommended against a group of leaf-eating pests of cabbage, fruit trees, gardens, parks, and forests. The microbiological method of control consists in the use of cultures of pathogens in formulations suitable for the practical dissemination of infection in pest populations.

Biological agents are characterized by the following positive qualities: the specific action of most insect pathogens, their harmlessness to beneficial insects and mites, their low toxicity to humans and warm-blooded animals, their compatibility with many chemical pesticides and other means of pest control, the low doses for

treating plants, and the absence of residues dangerous to humans in the processed farm products. The use of biological agents is especially promising for protecting vegetable, fruit, and fodder crops where chemical treatments are limited owing to the danger of the accumulation of pesticide residues.

In controlling harmful insects, the use of bacterial and fungal formulations mixed with small doses of insecticides deserves attention. These mixtures are highly effective in controlling pests such as the beet weevil, the Colorado beetle, and the gypsy moth.

When insecticide-microbe combinations are used, the consumption of the biological agents and insecticides is reduced in comparison with their separate application, the development of the disease in insects weakened by the insecticide and the total toxic action of the insecticide and the toxins produced by the microorganisms is more positive, and a high effect is achieved with a broader range of temperature and humidity fluctuations (for instance, of insecticide-bacterial combinations at low temperatures, and of insecticide-fungal combinations in arid conditions) when the separate application of fungal and bacterial formulations is not effective.

The use of insecticide-microbe combinations leads to weakening of the protective reactions of pests to entomophags.

11.1. Bacterial Agents for Controlling Harmful Insects

The main way of artificially causing bacterial diseases of insects is the overall application of pathogenic bacterial agents to the territory populated by pests.

Insects are killed by bacteria of over 90 species among which are obligate and facultative parasites.

The greatest practical successes have been achieved as a result of application of spore-forming bacteria of the group *Bacillus thuringiensis* against the leaf-eating species of *Lepidoptera*. A feature of these bacteria is the formation in the cells, in addition to spores, of crystalline inclusions containing substances toxic to insects. The strains separated from the group *Bacillus thuringiensis* with respect to their antigenic properties are divided into five serological types differing in their nature and spectrum of action. The spore-forming bacteria *Bacillus popiliae* and *Bacillus lentimorbus* are used successfully for controlling the Japanese beetle.

Non-spore-forming entomopathogenic bacteria are used to a substantially smaller extent, which is associated with the insufficient development of ways of retaining their vitality.

Positive results have been obtained in tests involving the use of bacteria of the genus *Pseudomonas* to control leaf roller and gypsy moths, the *Bacterium prodigiosum* to control turnip moths, beet

weevils, pine moths, and the *Enterobacter Cloacae* to control locusts. To date, however, practical recommendations for the use of these bacteria have not yet been worked out.

At present in the USSR, three bacterial control agents against insects and one against rodents are recommended for use in agriculture and silviculture.

Entobacterin. The active ingredient consists of live spores and toxic protein crystals of the endotoxin of the bacterium *Bacillus thuringiensis var. galleria*. The culture of the bacterium was separated from the bee moth. Entobacterin is available in the following formulations:

a dry homogeneous light-gray powder with a moisture content of not over 4%, a titre of at least 30 000 million (one gram of the formulation contains at least 30 000 million spores and the same number of protein crystals of the endotoxin);

a paste with a titre of at least 50 000 million; a dry concentrate without a filler with a titre of at least 220 000 million;

a dry concentrate with an adhesive and a titre of at least 220 000 million.

The formulation may be stored for two years at a temperature from —30 to +30 °C. Entobacterin is very sensitive to an increase in the humidity, therefore it must be kept in premises with a relative air humidity not exceeding 60-70%, especially at high positive temperatures. It must be stored away from pesticides.

Entobacterin has a low toxicity to humans and warm-blooded animals (LD_{50} is over 10 000 mg/kg). The maximum tolerated concentration in the air of the working zone is 3 mg/m^3. The tolerance level in farm products is not regulated. The harvest time for agricultural crops is five days. The protective measures are the same as when working with a non-toxic dust. Entobacterin is harmless to plants and beneficial insects; it is used in a combination with insecticides, acaricides, and fungicides.

The formulation is ingested into an insect's organism together with its food. If the amount of absorbed protein endotoxin is sufficiently high, the insect rapidly (during one day) dies. At smaller doses, only paralysis is observed, but the insect stops feeding and therefore can cause no harm to plants. In the insect's intestine, bacteria begin to reproduce from the spores, they fill the tissues, and the insect dies because of general infection. As a result of weakening of the insect under the influence of the endotoxin, the usual intestinal microflora also becomes active and pathogenic. The resistance of various species of insects to entobacterin varies and depends on the composition of the intestinal microflora. This is why various rates of use of the substance are needed for different species of pests.

Entobacterin is effective against more than 50 species of leaf-eating pests of vegetable, fruit, and berry crops, gardens, parks,

and forests. Ermine and smoky moths, loopers, and white butterflies are the least resistant to it. Noctuid moths have a relatively high resistance.

Entobacterin may be applied during any period of vegetation, including blossoming and harvesting. The rates of use of the formulation and the concentration of the suspension depend on the temperature, the pest species, and the crop, and also on the apparatus used. The optimal temperatures are 20-30 °C and higher. At a temperature below 17 °C, its effectiveness lowers, and the rate of use must be increased. At a day temperature of 13-14 °C, treatments should be discontinued, or the rate of use doubled with the addition of pesticides in reduced doses. In the Northern Caucasus, Transcaucasus, and Central Asia, the rate of use of the formulation for spraying vegetable crops is 1 kg/ha with a suspension concentration in fine-drop spraying of 0.1-0.2%; for fruit and berry crops, gardens, and parks, the rate is 2.5 kg/ha, and the suspension concentration is 0.5%; in regions with lower temperatures and frequent rainfall, the rates of use in gardens are increased to 5 kg/ha with a suspension concentration up to 1%, while to control pests of cabbage and other vegetable crops the rate is up to 2.5 kg/ha with a suspension concentration in fine-drop spraying of 0.5%. The liquid is used at a rate of 400-500 litre/ha.

A prepared working suspension must be used immediately because its effectiveness lowers when stored for two or three hours. Cold water should be used when possible to prepare the suspension to ensure that non-germinating spores get onto the plants. Spraying is performed in the period of development of actively feeding caterpillars, preferably of the younger ages. Treatment should be carried out in the same hours as conventional chemical treatments; if there is no danger of sun burns, any time of the day is suitable.

Entobacterin applied to plants retains its activity from 8 to 10 days, after which the activity gradually diminishes during 1-1.2 months. The dose of entobacterin can be reduced by using it in combination with decreased (from 4 to 10 times) doses of pesticides (carbaryl, trichlorfon, dicofol) causing physiological weakening of the insects.

Dendrobacillin. The active ingredient consists of live spores of the crystal-forming bacterium *Bacillus dendrolimus* F. whose culture was separated from caterpillars of the pine moth. The control agent is a dry homogeneous powder of a light-gray or grayish-pink colour with a titre of at least 30 000 million. Its moisture content is up to 5%. It must be stored in dry cool premises away from insecticides. The storage period is 12 months. Dendrobacillin gives good results when food is infected. It is effective against numerous insect pests such as cone moths and pine loopers, brown-tail and cabbage moths, large white butterflies, and a number of harmful *Lepidoptera*

in gardens. It is mainly intended for controlling moths and worms on cotton: bollworms, turnip moths, and armyworms, and is used in combination with carbaryl. The rate of use is 2 kg of dendrobacillin and 0.3 kg of an 85% wettable powder of carbaryl per hectare. To prepare the working liquid, the dendrobacillin is mixed in a small amount of water, then the latter is added to the required amount (rate of use), after which the carbaryl is introduced. It is best to perform spraying early in the morning in good weather or in the evening. Good results are obtained from two-fold treatment.

The toxicological and hygienic characteristics are similar to those of entobacterin.

In connection with the fact that dendrobacillin is used in combination with carbaryl, the harvest time for cotton is 20 days.

11.2. Fungal Agents for Controlling Harmful Insects

Over 530 species of microscopic fungi causing diseases of insects are known. Infection with fungi mainly occurs through the integuments of insects' bodies, and to a smaller extent with their food. Of great significance in limiting the population of harmful insects and the origination of mass diseases are entomophthorous fungi of the class of phycomycetes. They are specialized parasites and kill insects of 12 orders. Fungi cause mass diseases of locusts, brown-tail moth caterpillars, pine noctuids, diamond back moths, grapevine and other scale, various species of aphids, apple tree leaf hoppers, etc. They can scatter their conidia over considerable distances, which facilitates the rapid spreading of the infection, and are capable of surviving in unfavourable ecological conditions even in the absence of the objects infected owing to the presence of dormant phases in their development cycle.

Muscardine fungi relating to the class of imperfect ones are encountered widely in nature. Mass diseases of insects caused by these fungi are observed quite often. The prerequisites for their development are weakening of the population and favourable conditions (temperature, humidity) of the environment. One of the most widespread pathogens of this group is the fungus beauveria, infecting about 175 species of insects, including apple worms, stalk borers, Colorado beetles, and pentatomids. The green muscardine fungus infects 75 species of insects whose pre-imago stages of development are associated with the soil.

Among the fungal agents, beauverin is recommended for plant protection.

Beauverin. This control agent is a white powder consisting of conidiospores of the white muscardine fungus *Beauveria bassiana* Vuill and a kaolin carrier. One gram of the agent contains from

2000 to 6000 million spores of the fungus causing the insect disease white muscardine. Beauverin must be stored in premises at a humidity of the air not over 70% and a temperature from 15 to 18 °C. The storage period of beauverin in these temperature and humidity conditions does not exceed six months. It is especially sensitive to an increased humidity because the swelling and germination of the fungus spores in these conditions leads to their losing vitality and to lowering of the activity of the agent. Beauverin may be used in combination with most insecticides and acaricides. Its combination with fungicides is prohibited. It has a low toxicity to humans and warm-blooded animals (LD_{50} is over 15 000 mg/kg), but when it gets into the respiratory tracts in the production of the formulation, the spores of beauverin cause allergic diseases in some people. It has slight cumulative properties. The maximum tolerated concentration in the air of the working zone is 0.3 mg/m^3. The tolerance level in farm products is not regulated. The harvest time is 20 days.

Upon germination, the fungus *beauveria* penetrates through the cuticle of insects into the hemolymph. In this connection, plants must be treated so that the formulation gets onto the bodies of insects. When beauverin is applied, insects perish as a result of toxicosis, because of the active development of the fungus in the bodies of the insects, and because of the growth of the mycelium in the hemolymph and the tissues. The effectiveness of beauverin may also manifest itself in its aftereffect: the infected insects perish in subsequent stages of their development (pupa, imago). The formulation may lower the fertility of insects and their resistance to low temperatures in winter. Beauverin can act as a stomach toxicant. It kills weakened insects, therefore it should be used in combination with small additions of insecticides. It is most effective to use beauverin in humid conditions at a temperature of 20-27 °C. The combined application of beauverin with insecticide additions is effective in arid conditions at a temperature of 20 °C.

To control the Colorado beetle, beauverin is applied by spraying crops with a suspension mixed with small doses of trichlorfon. The components are mixed when preparing the working suspension. The dose of beauverin is 1-2 kg and of 80% trichlorfon (the technical product or wettable powder) is 0.4 kg/ha. The rate of use of the working liquid in conventional ground spraying is 450, and in low-volume spraying, 135-150 litre/ha. Two treatments are needed: the first in the period of the beginning of the mass appearance of second-age larvae, and the second in 12 or 14 days after the first one. The harvest time is 20 days.

The use of beauverin in combination with small doses of insecticides ensures the death of 90-96% of the larvae of Colorado beetles. The vitality of beetles developed from larvae infected with the

fungus diminishes appreciably, and 95-97% of such beetles perish during the winter.

BIP. The active ingredient consists of the live spores and insecticidal crystals of the bacterium *Bacillus thuringiensis var. caucasicus.* BIP is formulated as a dry powder or a liquid substance. The titre is at least 30 000 million spores and crystals in one gram. It is harmless to humans and warm-blooded animals.

The storage period is one year at not over 40 °C.

It is recommended for controlling pests of cabbage and fruits with ground spraying using aqueous solutions having a concentration of 0.5-1% and a dose of the formulation of 2.5 kg/ha.

11.3. Bacterial Agents for Controlling Rodents

The microbiological method of controlling harmful rodents is based on the artificial infection of the animals with pathogenic microorganisms.

Practical use has been found by bacteria of the genus *Salmonella*, pathogens of typhoid diseases of rodents. Among these bacteria, those of Merezhkovsky (*Salmonella typhi spermophilorum*), of Isachenko (*Sal. decumanicidum*), and No. 5170 of Prokhorov (*Sal. typhimurida rodentia*) have been studied in detail. Cultures of the first two species were separated from ailing rodents (gophers and brown rats) during a natural epizooty at the end of the 19th century. The bacterium of Prokhorov was obtained experimentally upon the multifold passage of strains of the bacillus coli communis on a conventional nutrient medium. All the indicated bacteria are specific to rodents.

The artificial infection of rodents at the places of their concentration may lead to the setting up of prolonged sites of infection. In favourable conditions, epizooties may develop on treated and adjacent sections. For an epizooty to develop among rodents, of great importance are contacts of healthy specimens with ill ones. With considerable isolation of the rodent habitats and diminishing of the contacts between them, the possibility of infection on a large scale decreases.

It has been established that with the aid of Isachenko's bacteria, which are the main ingredient of bactorodencide, artificial sites of epizooties can be set up in places inhabited by the common vole. As a rule, at these sites from 40 to 80% of the voles are infected as a result of contact with their ill companions. Such an artificially induced epizootic process does not last long, in one or two months it attenuates because the main part of the population involved in the epizooty dies, while the remaining animals acquire an increased resistance to the pathogen. It has been established that rodents have a special mechanism of immunity to bactorodencide. Par-

ticularly, a major role in protecting rodents' organisms from pathogenic bacteria is played by lysozime and similar substances present in the blood, liver, spleen, and other internal organs. On some bacteria, lysozyme has a bactericidal action, on others, a bacteriostatic action, while on third ones it acts as a mutagen or inducing agent causing variation of a bacterial cell or releasing of its prophage and conversion of it into a virulent form.

Bacterial agents do not put rodents on their guard and are readily eaten by them with food bait. The bacteria when ingested with food act on the thin section of the intestine and the spleen of the animals. Development of the disease and death take place gradually. From 3 to 20, and sometimes up to 30 days elapse from the instant of infection to the appearance of the first symptoms of the disease and death of the rodents.

Bactorodencide. The active ingredient consists of bacteria of rodent typhus (Isachenko's bacteria) relating to the genus *Salmonella*. This agent is available in two formulations.

Dry granular bactorodencide consists of grains with bacteria dried on them. The titre is at least 1000 million. The moisture content of the grain is 14%.

The lethal dose of the agent for the species of mice and voles susceptible to it is contained on two to four grains. The formulation must be stored in dry premises away from toxic substances. The storage period is one year at a temperature from −25 to +22 °C and three years from −25 to +4 °C.

Dry aminobone bactorodencide has the form of a coarse-grained loose gray substance. Its moisture content is 6% and its titre is at least 100 million.

The granular formulation is used against common and bank voles, and the aminobone formulation is used against common, bank, water voles, house mice, black and gray rats. Both formulations give the best results in the early or late spring when the rodents gather in separate places. The dose of granular bactorodencide depends on the species, number of rodents, and the kind of habitat treated. When controlling mice and voles on fields, meadows, and in gardens, the dose is 1-2 kg/ha, in stacks of grain and the like it is 5-30 g/m^3, in hotbeds, stores, livestock farms and dwellings, it is 0.5-1 g/m^2. The dose against rats in open habitats is 500-2000 g/ha, and in closed ones it is 1-2 g/m^2. The granular formulation is used without the addition of bait products. Before applying the dry aminobone bactorodencide, it is subjected to reactivation for restoring the vital functions of the bacteria contained in it. For this purpose, warm (30-35 °C) boiled water is added to the formulation 10 to 12 hours before use in the ratio of 1 : 1. During this time, the wetted substance is stirred two or three times and kept in warm premises. In the course of reactivation, the titre reaches 8000-10 000 million.

After reactivation, the formulation is well mixed with a double amount of bait (flour, groats, crushed grain, finely minced vegetables, potatoes, etc.). The prepared bait is placed into the burrows, near them, and along the paths used by the rodents.

The granulated aminobone formulation is used without bait and is not reactivated. The dose of the dry formulation for infecting one mouse or vole is 0.1-0.2 g, and one rat is 0.3-0.5 g.

In controlling mice and voles on fields, pastures, meadows, and in gardens, the rate of use of the powdered formulation is 100-200, and of the granulated one is 250-500 g/ha. The control of these rodents in stacks of grain and the like requires 0.5-1 g/m^3 of the powdered or 1-5 g/m^3 of the granulated formulation. In hotbeds, stores, livestock farms, and dwellings, the powdered formulation is used at a rate of 0.05-1 g/m^2, and the granulated one at a rate of 0.1-1 g/m^2.

11.4. Biological Control of Plant Pathogens (Antibiotics)

The studying of antibiotics as a means of controlling plant diseases was begun comparatively recently. The possibility in principle of using them to control some plant diseases was proved in the fourties. The widespread investigation and the practical use of such substances relate to the fifties.

At present, the expediency has been proved of using antibiotics to control a number of diseases (burning of fruit trees caused by *Erwinia amylovara*, pyriculariosis and other diseases of rice, bacterioses of beans, soybeans, and certain virus diseases) against which there are no sufficiently effective chemical fungicides. The prospects of employing antibiotics are due to their following properties:

their comparatively low toxicity to humans and animals;

their ability to penetrate into plants and increase their resistance to diseases;

the specific nature of their action;

their high activity with respect to the pathogenic organisms, which allows them to be used in very small concentrations and avoid the accumulation of their residues in products and the soil. Most antibiotics in definite concentrations stimulate the growth and development of plants and increase the yield.

Antibiotics may be combined with other fungicides.

Arenarin. This is an antibiotic of a vegetative origin. The substance is prepared from dry flowers of sand immortelle (*Helichrysum avenarium*). Arenarin effectively controls the development of various phytopathogenic bacteria. An especially strong inhibiting action has been noted with respect to the pathogen of bacterial cancer of tomatoes.

It is recommended for the preplanting treatment of tomato seeds against bacterial cancer. This treatment of the seeds also facilitates the reduction of infection of the plants with black bacterial spot, soft blossom-end rot and other rots, and also with virus diseases. The seeds are wetted in an aqueous solution of arenarin with a concentration of 1 : 1000 and are kept in it for 2.5 hours. To treat one kilogram of seeds, 100 ml of the liquid formulation of arenarin are needed. The working solution for wetting the seeds is taken with a surplus in a dose of 5 litre/kg of seeds. After being wetted, the seeds are spread out in a thin layer and dried. The formulation has a low toxicity to humans and warm-blooded animals (LD_{50} for mice is 3000-4000 mg/kg).

Phytobacteriomycin. This antibiotic is the product of vital activity of an actinomycete from the group *Actinomyces lavendula*. The formulation is available with an activity of 20 000 unit/g. It is a cream-coloured or light-brown powder well soluble in water. Phytobacteriomycin is moderately toxic to humans and warm-blooded animals (LD_{50} for rats when ingested orally is 550 mg/kg, for mice is 320 mg/kg, and for guinea pigs is 158 mg/kg). The formulation has a moderate ability of cumulation, with a cumulation coefficient of 1.9. It has an irritating action on the skin and mucous membrane of the eyes. Phytobacteriomycin is recommended for the preplanting treatment of seeds against the bacterial burning of beans and soybeans. Soybean seeds are treated with phytobacteriomycin by powdering with the dust on the day of planting at a rate of 3 g/kg of seeds. The maximum tolerated concentration in the air of the working zone is 0.002 mg/m^3. Treated soybean seeds must never be used in food.

Trichothecin. The active ingredient is an antibiotic produced by the vital activity of the fungus *Trichothecium roseum*. It has fungistatic and fungicidal activity. It is marketed in the form of the pure substance—a yellow crystalline solid insoluble in water with an activity of 750 unit/mg. It is well soluble in organic solvents. It is also available as a 10% wettable powder.

Trichothecin is moderately toxic (LD_{50} for laboratory animals is 263-400 mg/kg). Its cumulation coefficient is 7.

The tolerance level in cucumbers is 1 mg/kg. The maximum tolerated concentration in the air of the working zone is approximately 0.2 mg/m^3.

It is used to control true powdery mildew and root rots.

It is highly effective in controlling powdery mildew of cucumbers in sheltered soil. The plants are sprayed with a 0.02% solution of the pure substance or a 0.4% suspension of the dust. The dose per hectare is 200 g of the 10% dust. The latter is dissolved in acetone to a creamy paste, and then water is added up to 500 litres. The wetting agent OP-7 must be added to the working liquid in an

amount of not over 5 ml per 10 litres. The cucumbers are sprayed two to four days before the appearance of the powdery mildew or when its first symptoms are observed. If the disease does not develop after the first treatment, the second one may be performed not earlier than in 15 days. If powdery mildew appears again after the first treatment, the second one must be performed in 3-5 days and repeated subsequently two or three times.

Trichothecin has no negative effect on the *Phytoseiulus persimilis* widely used to control spider mites in sheltered soil. The harvest time is three days, and washing of the products with water is obligatory.

Chapter 12

REGIONAL USE OF PESTICIDES

12.1. Selection of Pesticides Depending on Specific Composition of Pests

The selection of a pesticide in concrete conditions depends on the specific composition of the pests, and on the state and the density of their population. Pests of agricultural crops must be considered with a view to the harm they cause to the crop. The harm depends on when the pests appear, their number, and the stage of development of the crop. To determine the real danger to agricultural crops of potentially harmful species, it is necessary to conduct regular geographical, ecological, and economical investigations. This will make it possible to determine the composition of the species that are most dangerous to each crop. For each species, it is necessary to establish the regions or zones where the use of chemical means of protection is economically expedient.

First of all, it is necessary to use pesticides such that will make it possible to successfully control polyphagous and especially dangerous pests and quarantine objects.

The main seats of the mass reproduction of swarms of locust pests are concentrated in the steppe and semidesert regions. Locusts are controlled at present by dusting or spraying the territory they occupy with HCH, parathion-methyl, or malathion.

The greatest harm by wireworms is observed in the non-chernozem region of the European part of the USSR, and especially in the forest-steppe region. The main way of chemical protection against wireworms is dusting of the seeds with HCH or heptachlor before planting them.

The regions of the greatest harm caused by codling moths are the Crimea, the south of the Ukrainian SSR, and the Moldavian SSR. Here preference should be given to phosalone, tetrachlorvin-

phos, or phenthoate as the most effective pesticides for controlling this pest.

In the North Caucasus, the Volga River zone, and the forest-steppe regions of the Ukrainian SSR, pentatomids are a dangerous pest of wheat. Consequently, parathion-methyl, trichlorfon, and fenitrothion must be used in these regions.

To control aphids (vectors of virus diseases of cotton, sugar beets, and potatoes) in the Uzbek, Ukrainian, and Moldavian republics, the greatest favour should be given to menazon, a pesticide having a low toxicity to humans, harmless to beneficial insects, and highly effective in controlling aphids.

Mercurbenzene is intended for disinfecting seeds in all the regions of the USSR.

Dinocap is the most effective against powdery mildew of cucumbers in sheltered soil and, consequently, will be used in greenhouse and hotbed farms.

Dichlofluanid provides reliable protection of grapevines and strawberry plots against gray rot in Moldavia, the Ukraine, North Caucasus, and Transcaucasus.

Carboxin is a systemic pesticide that is most effective against loose smut of wheat and barley and may be applied in the main regions of cultivation of these crops.

In some regions of Kazakhstan and the Altai territory, wheat fields are highly contaminated by wild oats. Consequently, in these regions, herbicides effective against this weed (barban, tri-allate, benzoylprop ethyl) must be used in combination with a system of agrotechnical procedures.

Bare slugs harm various crops. They are widespread in the European part of the USSR, but cause especially great harm in the zone of excessive moisture. To control bare slugs, which cause the greatest harm in this zone, metaldehyde is recommended.

The harmful activity of gophers is mainly observed in the steppe regions of the RSFSR, Ukraine, and Kazakhstan. The main way of controlling gophers is the scattering of grain baits with zinc phosphide. This formulation must be applied in the regions of the greatest dissemination of these rodents.

Milbex can be used to control mites on various crops in different regions of the country. Since the resistance of mites to this pesticide appears considerably more slowly than to other ones, it is recommended for controlling spider mites on cotton in regions where the resistance of this pest to other acaricides has been noted.

Pesticides should be used with a view to the economical threshold of harmfulness of pests, i.e. at a population of the pest when the harm it causes is felt economically, and the cost of the chemical measures for controlling it is rapidly justified. For example, it is expedient to use pesticides against pentatomids on cereals if there is

an average of 0.5-1 adult bug or over two of its larvae per square metre of field. The main task in controlling ordinary spider mites is to prevent its mass reproduction on cotton fields. Therefore, the first treatment with pesticides must be performed already when 1% of the plants are found to be populated by the mite. Repeated chemical treatments are needed if the development of the cotton is retarded; their use and periods of application depend on the effectiveness of the first treatment.

12.2. Prediction of Pest Dissemination and Development—the Basis of the Rational Use of Pesticides

The basis for planning the use of chemical means of plant protection is the prediction of the probable appearance and spreading of pests, diseases, and weeds. This makes it possible to determine the crops and planted areas on which chemical measures must be taken, choose the pesticides properly, and calculate their amount.

The working out of long-term predictions of the appearance and dissemination of pests is aimed at determining the species to be controlled and, consequently, at planning the periods of application of the pesticides.

The application of pesticides to control certain species of pests in a specific soil and climatic region is usually associated with definite, already established, periods or seasons. For example, the fumigation of seeds and planting stock, the preplanting treatment of seeds with insecticides or combined formulations, the early spring combined prophylactic treatment of orchards against wintering stages of pests and pathogens, and the spring control of gophers require no special signals.

But for the successful chemical control of very many pests, it is necessary to establish accurate dates for the beginning and end of pesticide application and recommend the ways of application. This is associated with the fact that many pests and weeds are vulnerable to pesticides only during a limited time and only in definite stages of ontogenesis. For instance, the San Jose scale is best controlled by insecticides in the mobile larva stage, hence contact insecticides are most effective in this period. The use of chemical formulations is often safe and harmless to the crop being protected only in definite stages of plant development. Finally, the cost of chemical plant protection may be justified economically only at a definite level of the harm to the crop that may be caused by pests. For this purpose, regular observations are needed of the state of the harmful organisms and the crops being protected in specific soil and climatic regions.

12.3. Tasks and Principles of Zoning When Using Pesticides

The development of a system of chemical measures aimed at controlling the main harmful species on a crop or in a given region, and also the planning of expenditure on these measures are based on zoning the country's territory with respect to the dissemination of the harmful species. Such zoning is also essential to understand the changes in the composition of the harmful flora and fauna that will occur subsequently upon the regular use of pesticides.

In zoning the use of pesticides, it is first of all necessary to take into account the area of the crop being harmed. For example, molinate used to kill weeds on rice fields will be applied in regions where rice is grown. Diquat is used to control weeds in growing crops with minimum cultivation in Kazakhstan and the Altai territory. Copper trichlorophenolate is used to protect cotton seeds against bacterial blight and other diseases. Consequently, it is used only in regions where cotton is grown. Similarly, hexachlorobutadiene, which is recommended for controlling vine lice, is used on grapevines infected with this pest. The region occupied by a crop, however, may be considerably wider than that in which a given pest causes harm, therefore the same formulation may be used in different soil and climatic zones.

Of great importance are also soil and climatic factors, which may influence substantially the effectiveness of pesticides. Formulations of elementary sulphur (ground sulphur, etc.) are known to be sufficiently effective in controlling powdery mildew on various crops and mites only at relatively high temperatures (25 °C and above). Consequently, it is good to use sulphur mainly in the southern regions of the USSR and in regions of other countries with a warm climate. It should be used elsewhere only in years with a relatively high temperature of the air.

A pesticide must never have an adverse influence on the plant being protected. The main determining factors here are the temperature, humidity, and the species and variety of the plant. For example, the phytocidal properties of copper-cased formulations are affected noticeably by the humidity. Bordeaux mixture and copper oxychloride in some years with a high humidity cause burning of the leaves. Therefore, attention must be given to the features of the species and varieties of the plants. In the same conditions, different species and varieties of plants react differently to the action of pesticides.

The application of pesticides must not have a harmful aftereffect on a biocoenosis. It is general knowledge that plants treated with zineb or captan are more susceptible to powdery mildew than plants on which these pesticides were not used. For this reason in regions

with powdery mildew, folpet must be used on fruit trees instead of captan, while on grapevines it is good to use copper oxychloride or combined formulations based on it such as cuprosan, and also formulations based on sulphur.

When applying pesticides, it must be remembered that their rates of use are different in various soil and climatic zones. It is known that in the preplanting dusting of seeds in arid regions, less HCH is used than in regions with sufficient moisture. The rates of use of soil herbicides (simazine, atrazine, etc.) on chernozem and clay loamy soils are higher than on podzolic and sandy ones.

This is why pesticides must be applied with a view to the recommendations of the zonal scientific-research institutions of the country.

Whether or not to use pesticides must in all cases be determined proceeding from the specific farm conditions and the economical expediency. All work connected with the use of toxicants must be performed in strict accordance with the safety rules in force.

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[1] Trade (brand) names are indicated by one asterisk (*), names used only in the USSR—by two asterisks (**). The names with no asterisks are common ones approved by the relevant standards institution. Page numbers set in bold-face type indicate where the chemical name, formula, and/or detailed description of the pesticide are given.

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